



# COLLOID CHEMISTRY





# COLLOID CHEMISTRY

## *Principles and Applications*

By

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FOURTH EDITION



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Thou can'st learn something from everyone. Be not arrogant because of thy knowledge, and have no confidence in that thou art a learned man. Take counsel with the ignorant as with the wise, for the limits of art cannot be reached, and no artist fully possesseth his skill. A good discourse is more hidden than the precious green stone, and yet it is found with the slave-girls over the mill-stone."

*The first of the Maxims of Ptah-hotep, Vizir of King Issi, written in Egypt about 2675 B. C.*

"Those rules of old discovered, not devised,  
Are nature still, but nature methodized;  
Nature, like liberty, is but restrained  
By the same laws which first herself ordained.

*Essay on Criticism—Alexander Pope.*

"Trace science then, with modesty thy guide;  
First strip off all her equipage of pride;  
Deduct what is but vanity, or dress,  
Or learning's luxury, or idleness;  
Or tricks to show the stretch of human brain,  
Mere curious pleasure, or ingenious pain. . . .

*Essay on Man—Alexander Pope.*

"I am a part of all that I have met;  
Yet all experience is an arch where thro'  
Gleams that untravell'd world, whose margin fades  
Forever and forever when I move . . .  
To follow knowledge like a sinking star,  
Beyond the utmost bound of human thought . . .  
To strive, to seek, to find, and not to yield."

*Ulysses—Lord Tennyson.*



## PREFACE TO FOURTH EDITION

In preparing this greatly enlarged fourth edition, the author has adhered to the principles which governed the preparation of its predecessors: (1) assemblage of experimental data into naturally coordinated and interlocking groups, to form a broad mosaic which gives a coherent picture of nature; (2) breaking down the artificial mental barriers arising from scientific specialization and its incidental Babel of scientific jargon, so that the resources of many fields of investigation may be considered and both breadth and depth of mental focus acquired.

The book is built around no one theory. Observable facts are stressed, theoretical considerations being incidentally invoked so that the facts may be better coordinated and their import understood. Nearly a century ago Liebig remarked to Wöhler that there was no lack of experiments and facts, but in understanding what they mean. And Wellington, addressing an officer whose report was replete with undigested details, blurted out: "Sir, your information is too great for your understanding."

Experimental facts, the building blocks of science, may be assembled into a variety of theoretical structures. It is futile as well as unscientific to build or to support a theory with hand-picked facts selected *ad hoc*, while opposing or non-conformist facts are slighted or forgotten. In order to be saved a theory must be all things to all pertinent facts. Data collected in diverse, highly specialized, and apparently isolated fields are often found to have an aidful or a disruptive influence on a theory, necessitating its modification or its abandonment. While the facts of science are usually developed by successive steps, the theoretical advances forced by new facts are often of a revolutionary nature.

To make the book more useful as an adjunct to teaching, the greatly enlarged content has been rearranged coherently along the lines of a text. But no attempt has been made to emulate the dour dogmatism and paucity of interest once deemed essential by those who as students acquired, and as teachers perpetuated, the text-book mind. The attempt is made to humanize the bare

skeleton of scientific principles by using numerous practical illustrations, so that interest may aid memory and knowledge be painlessly acquired. The book should therefore appeal to the student, and, despite a few mathematical expositions, to the general reader as well. To those interested in biology and medicine, the book offers a preliminary glance into many borderline fields, and consequently a certain degree of orientation in their chosen work. Appreciation of the principles and applications of colloid chemistry in all fields of pure science and technology continues to develop, as is evidenced by the ever-increasing literature, and by the fact that special courses or series of lectures on colloid chemistry are being established in an ever-increasing number of educational institutions. The reader is urged to keep abreast of the current literature, but not to forget that a great wealth of information is stored up in the literature of the past. The most recent work is not necessarily the best—or even new. Papers published long ago may be surprisingly accurate, and may contain observations not noted by later experimenters in the same field. Errors do not become facts just because they are put into print.

Nor should it be forgotten that truth must be accepted, no matter what its source, and a supercilious attitude toward “practical men” must be avoided. Furthermore, truth suffers if scientific inquiry is trammelled by pedagogical limitations. It is hoped that the consideration given certain matters not commonly considered from the colloid-chemical point of view, will be helpful in illuminating items generally referred to by teachers in the colloid field.

The author is greatly indebted to many scientific colleagues for reprints, information imparted, and critical suggestions, but he assumes full responsibility for any views expressed. He also thanks various editors and publishers for permission to reproduce illustrations. Where possible, proper credit is given locally throughout the book, and a large number of references to the literature are given in like manner. For the convenience of the reader, a glossary of the less familiar terms is appended, and the manual of simple experiments introduced into the last edition is continued.

JEROME ALEXANDER

New York, February, 1937.

## PREFACE TO THIRD EDITION

To meet the increasing demand for this little book, there has been prepared a Third Edition, greatly enlarged in both the theoretical section and in the practical applications. An Appendix has been added giving some experimental suggestions which constitute a modest laboratory manual, based mainly on materials and apparatus readily obtainable in the kitchen or household, or else at any drug store. The Appendix describes many simple experiments which go directly to the root of the principles involved. Montaigne once said that he liked peasants, because they were not sufficiently educated to reason incorrectly.

If any purist of pedagogic tendencies were to point out that the book includes items and data not strictly of colloidal nature, it may be said that Nature, herself, is delightfully oblivious to definitions, rules, laws, metes and bounds established by scientists for their own convenience. And often what might in strictness be considered as extraneous matter may add interest, zest and a background which leads to better appreciation of material unquestionably pertinent.

It is interesting to compare the 1907-1916 Decennial Index of "Chemical Abstracts" with the 1917-1926 Decennial Index; for this comparison indicates, although it by no means measures, the great increase of interest in colloid chemistry during the decade. The former Index contains only twelve columns of titles under "Colloids," while the latter contains twenty-seven columns under that heading alone, besides a very great number of other papers dealing with colloid phenomena, indexed under such headings as "adsorption," "Brownian movement," "disperse systems," "gelatin," "micelles," "particles," "ultra-filters," etc.

The author gratefully acknowledges his indebtedness to very many writers and experimenters whose names and works are often mentioned specifically. While some of the ideas advanced are believed to be novel, no claim of priority is made or implied; for what is of most importance to the advance of science is not



"*Who is first, right?*", but "First, *what* is right?". And there is usually some divergence of opinion as to what *is* right. The older literature abounds in forgotten or over-looked work of importance, some of which, despite the fact that it may have appeared long in advance of its time, has a surprisingly modern aspect. Frequently, things which we have seen, heard or read, and then apparently forgotten, lurk in our subconscious minds and influence our future thought.

JEROME ALEXANDER.

NEW YORK,  
November, 1929

## PREFACE TO SECOND EDITION

The favorable reception accorded the first edition of this little book has led the author to enlarge and extend greatly this second edition, both in the theoretical and the technical sections, so that it may be used as an adjunct in teaching colloid chemistry, if not indeed as a text book. A large number of new practical applications have been introduced, and the effort has been made to develop the subject in a simple, coherent, and interesting manner, using, as far as possible, non-technical language and homely illustrations, so as to enable the reader's interest to aid memory.

The growing realization of the importance of colloid chemistry is evidenced by the fact, that, whereas the Decennial Index of Chemical Abstracts covering the years 1907-1916 contains only twelve columns of titles under Colloids, the 1922 Index alone contains five columns, and the 1923 Index contains four columns. These figures do not include many germane papers which are indexed under such headings as Adsorption, Diffusion, Coagulation, Gelatin, Gel, Sol, and a wide variety of physical, biological, and technical topics; but they do show that the colloidal zone is no longer "the world of neglected dimensions" as Wo. Ostwald once called it.

Matter in the colloidal state has unique properties which necessitate a revision of some of our preconceived notions; and this fact cannot be avoided by attempting to alter definitions and the established meaning of language, or nullified by a Procrustean effort to fit all experimental data to existing theories.

To use a good old-fashioned term, we need *natural philosophers*, men whose view of the various fields of science is sufficiently broad and keen to enable them to see, understand, and correlate correctly apparently scattered facts in physics, chemistry, biology, technology, and related branches.

Science is not a sporting event. The true scientist's slogan is not "May the best man win," but rather "May the truth pre-

Colloid chemistry comes not to destroy, but to fulfill. It does not destroy or even replace the known facts of chemistry, physics, and other sciences, but draws attention to certain aspects of Nature which have often been overlooked.

JEROME ALEXANDER.

50 EAST 41st St.,  
N. Y. CITY,  
July 1, 1924

## PREFACE TO FIRST EDITION

This little book is the result of an attempt to compress within a very limited space the most important general properties of colloids, and some of the practical applications of colloid chemistry. Its object will be accomplished if it is helpful in extending the sphere of interest in this fascinating twilight zone between physics and chemistry.

J. A.

NEW YORK,  
November 1, 1918

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## CHAPTER I

### HISTORICAL AND INTRODUCTORY

LIKE all other divisions of science which have their roots deep in the basic nature of matter, colloid chemistry did not spring, like Minerva, full-armed and panoplied, from the front of Jove. It is true that Thomas Graham, Master of the Mint, the keen-witted Scotchman to whom both chemistry and physics owe so much, was the father of modern colloid chemistry; but he had many precursors, who saw more or less clearly that, when *any* kind of matter is reduced to extremely fine or submicroscopic particles, it thereupon acquires peculiar and unusual properties. And, when we realize that cooks, farmers, and artisans of all nations have, for untold centuries, been practical workers in colloid chemistry, we feel like M. Jourdain in Molière's comedy "Le Bourgeois Gentilhomme," when he found he had been talking prose all his life and exclaimed, as he was taught the wonders of elementary enunciation: "Vive la Science!"

An outstanding example of an ancient use of colloid-chemical principles is the manufacture of Chinese ink where gelatin is used to deflocculate the carbon black. India ink is a similar preparation, and it is probable that the ancient Egyptians used gum arabic (acacia) to deflocculate pigments in making inks. The *aurum potabile* of the alchemist was made by reducing gold chloride in the presence of ethereal oils. The purple of Cassius is a colloidal gold stabilized by stannic oxide. As far back as 1794 colloidal gold produced *in situ* was known as a silk dye. The ancient Egyptians used glue, as is evidenced by a drawing in the tomb of Rekmara at Thebes, where wood-workers are represented applying veneers of expensive wood to common sycamore, the glue being heated nearby and being applied with a brush. Colloid practices in the field of agriculture are mentioned by Hammurabi, *e.g.*, in the preparation and cultivation of the soil.

In 1925, the Colloid Committee of the British Association republished a number of important basic papers on Colloid Chemistry.\*

The first of these is a paper by Dr. Ascherson of Berlin presented to the Paris Academy of Science on November 12, 1838, in which he ascribes formation of emulsions to formation of a film around the emulsified globules, and in substance anticipated the ultramicroscopic form of illumination. In pointing out that if oil is shaken with water containing a trace of albumin, some of the oil droplets are coated while others are not, he stated, "the latter are best seen by focusing the microscope exactly on the surface of the liquid and illuminating from the side." The protective film he called the *haptogen membrane*.

Then follow two papers by Francesco Selmi of Bologna on *Demulsion of Silver Chloride*, presented in 1845, and *Pseudo-Solutions of Prussian Blue and of the Influence of Salts in Destroying Them*, presented in 1847.

Then follows a paper by Ascanio Sobrero, of Turin, and Francesco Selmi on the *Products of Decomposition of Sulphuretted Hydrogen and Sulphurous Acid in Aqueous Solution*, presented before the Academy of Science at Turin in 1849, wherein the authors remark that "the state of the sulphur can therefore be modified, in a peculiar manner, by the presence of bodies in the medium in which it deposits, which bodies it retains obstinately, probably by simple adhesion; and the sulphur may thus acquire the property of forming an emulsion, or a state of aggregation which prevents it from subdividing itself in water. It follows, in addition, that the emulsifiable sulphur presents phenomena analogous to those which can be observed in many other bodies having the property of dispersing or dividing themselves in a liquid without, however, absolutely dissolving in it, such as soap, starch or Prussian Blue, on which one of us, M. Selmi, has already made observations similar to those which we have here set forth. These phenomena belong to a class which M. Selmi has well characterized and has grouped together under the name of 'pseudo-solutions.' It would appear that the number of 'pseudo-soluble' bodies is fairly large. We have already undertaken some re-

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\* *The Foundations of Colloid Chemistry, Selections of early papers bearing on the subject*, edited by Emil Hatschek. (Ernest Benn, Ltd., London, 1925.)

searches on this subject, and the organic bodies in particular appear to us to be of great interest from this point of view."

Michael Faraday's important paper on the *Experimental Relations of Gold (and other Metals) to Light* ("Phil. Transactions" 1857, page 145) is given in part. Prof. Richard Zsigmondy, discoverer of ultramicroscopy, after having independently rediscovered many facts regarding colloidal gold, found Faraday's paper in making a thorough search of the literature and rescued it from the oblivion into which it had fallen.\*

Recently (see "Science," 1925, p. 184) the writer by chance discovered a practically forgotten book by Dr. William M. Ord, of St. Thomas' Hospital (Edward Stanford, London, 1879) entitled *On the Influence of Colloids upon Crystalline Form and Cohesion*, wherein many older observations are mentioned and much modern material may be rediscovered.

In a paper entitled "Remarks on Colloidal Silver" by Prof. Carl Barus (Brown University) in the American Journal of Science for December, 1894 (47, 451-4) foreshadowed many of the subsequent developments in colloid chemistry. (See note in "Science", 1927, 65, 301-2).

Although many facts and principles concerning colloids have from time immemorial been known and utilized empirically, the scientific foundation of modern colloid chemistry was laid by a Scotchman, Thomas Graham, F.R.S., Master of the Mint. In two basic papers on this subject, the first entitled "Liquid Diffusion Applied to Analysis," read before the Royal Society of London, June 13, 1861, the second entitled "On the Properties of Colloidal Silicic Acid and other Analogous Colloidal Substances," published in the *Proceedings of the Royal Society*, June 16, 1864, Graham pointed out the essential facts regarding colloids and the colloidal condition, and established much of the nomenclature in use at the present day. In the first of these papers Graham says: "The property of volatility, possessed in various degrees by so many substances, affords invaluable means of separation, as is seen in the ever-recurring processes of evaporation and distillation. So similar in character to volatility is the diffusive power possessed by all liquid substances, that we may fairly reckon upon a class of analogous analytical resources to arise

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\* "Colloids and the Ultramicroscope," J. Wiley and Son, 1909.

from it. The range also in the degree of diffusive mobility exhibited by different substances appears to be as wide as the scale of vapor tensions. Thus hydrate of potash may be said to possess double the velocity of diffusion of sulphate of potash, and sulphate of potash again double the velocity of sugar, alcohol and sulphate of magnesia. But the substances named belong all, as regards diffusion, to the more "volatile" class. The comparatively "fixed" class, as regards diffusion, is represented by a different order of chemical substances, marked out by the absence of the power to crystallize, which are slow in the extreme. Among the latter are hydrated silicic acid, hydrated alumina and other metallic peroxids of the aluminous class, when they exist in the soluble form; with starch, dextrin and the gums, caramel, tannin, albumen, gelatin, vegetable and animal extractive matters. Low diffusibility is not the only property which the bodies last enumerated possess in common. They are distinguished by the gelatinous character of their hydrates. Although often largely soluble in water, they are held in solution by a most feeble force. They appear singularly inert in the capacity of acids and bases, and in all the ordinary chemical relations. But, on the other hand, their peculiar physical aggregation with the chemical indifference referred to appears to be required in substances that can intervene in the organic processes of life. The plastic elements of the animal body are found in this class. As gelatin appears to be its type, it is proposed to designate substances of this class as colloids, and to speak of their peculiar form of aggregation as the colloidal condition of matter. Opposed to the colloidal is the crystalline condition. Substances affecting the latter form will be classed as crystalloids. The distinction is no doubt one of intimate molecular constitution.

"Although chemically inert in the ordinary sense, colloids possess a compensating activity of their own, arising out of their physical properties. While the rigidity of the crystalline structure shuts out external impressions, the softness of the gelatinous colloid partakes of fluidity, and enables the colloid to become a medium for liquid diffusion, like water itself. The same penetrability appears to take the form of cementation in such colloids as can exist at high temperature. Hence a wide sensibility on the part of colloids to external agents. Another and eminently

characteristic quality of colloids is their mutability. Their existence is a continued metastasis. A colloid may be compared in this respect to water, while existing liquid at a temperature under its usual freezing-point, or to a supersaturated saline solution. Fluid colloids appear to have always a pectous modification; and they often pass under the slightest influences from the first to the second condition. The solution of hydrated silicic acid, for instance, is easily obtained in a state of purity, but it cannot be preserved. It may remain fluid for days or weeks in a sealed tube, but is sure to gelatinize and become insoluble at last. Nor does the change of this colloid appear to stop at that point. For the mineral forms of silicic acid deposited from water, such as flint, are often found to have passed, during the geological ages of their existence, from the vitreous or colloidal into the crystalline condition.\* (H. Rose.) The colloidal is, in fact, a dynamical state of matter, the crystalloidal being the statical condition. The colloid possesses *Energia*. It may be looked upon as the probable primary source of the force appearing in the phenomena of vitality. To the gradual manner in which colloidal changes take place (for they always demand time as an element) may the characteristic protraction of chemico-organic changes also be referred. . . .

"It may perhaps be allowed to me to apply the convenient term dialysis to the method of separation by diffusion through a septum of gelatinous matter. The most suitable of all substances for the dialytic septum appears to be the commercial material known as vegetable parchment, or parchment-paper. . . ."

At the beginning of the second paper above referred to, Graham states: "The prevalent notions respecting solubility have been derived chiefly from observations on crystalline salts, and are very imperfectly applicable to the class of colloidal solutions." From this it may be seen that Graham appreciated the fact that all the laws of crystalloidal solutions could not be applied to colloidal solutions. In the case of crystalloidal solutions the dissolved substance is present in a state of molecular subdivision, and, according to the ionization theory, is in many cases dis-

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\* This statement clearly shows that Graham appreciated the fact that the same substance (here silicic acid) could exist in either the colloidal or the crystalloidal state. The erroneous contrary statement has often been made, even by authors who quote these very words of Graham.—J. A.

sociated into ions. With colloidal solutions, on the other hand, we have a lesser degree of subdivision, and the particles in solution are larger and more cumbersome. As Graham remarked, "The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules and whether the basis of colloidalilty may not really be this composite character of the molecule." This is today the idea generally accepted, although individual molecules may, in some cases, reach colloidal dimensions.

### COLLOID CHEMISTRY DEFINED

Colloid chemistry deals with the behavior and properties of matter in the colloidal condition, which, as we now know, means a certain very fine state of subdivision. While there are no sharp limitations to the size of particles in colloidal dispersions, it may in a general way be stated that their sphere begins with dimensions somewhat smaller than the shortest wave length of visible light, and extends downward well into dimensions which theory ascribes to the molecules of crystalloids. (See Table V, p. 56.)

The measurements of the particles (length, breadth, and thickness) may be of colloidal size in one, in two, or in all three of its dimensions. The particles of *one-dimensional colloids* are of flaky form, like mica; of *two-dimensional colloids*, thread-like; or rod-like; of *three-dimensional colloids*, approximating the spherical. Langmuir's work (Alexander's "Colloid Chemistry, Theoretical and Applied," Vol. I, p. 538) indicates that molecules may change their shape according to environmental conditions. We must therefore face the possibility that colloidal particles (which, if not molecules, are composed of molecules) may also undergo changes in shape, dimension, and outwardly directed surface forces, depending on conditions. (See also p. 98 regarding the mesomorphic states of matter).

### SUSPENSION VS. SOLUTION

With the aid of the ultramicroscope, which renders visible particles approaching in minuteness molecular dimensions, Zsigmondy has shown that there is no sharp line of demarcation between suspensions and colloidal solutions, but that with increas-

ing fineness in the subdivision of the dissolved substance, there is a progressive change in the properties of the resulting fluids, the influence of gravity gradually yielding to that of kinetic motion, of the electric charge of particles, to surface tension and to other forms of energy. Thus in the case of metallic gold, subdivisions whose particles are  $1\ \mu$  and over act as real suspensions and deposit their gold, whereas much finer subdivisions ( $60\ m\mu$  and under) exhibit all the properties of metal hydrosols or colloidal solutions. In the ultramicroscope the coarser subdivisions show the well-known Brownian movement, which greatly increases as the particles become smaller, until at the present limit of ultramicroscopic visibility (about  $5\ m\mu$ ) it becomes enormous both in speed and amplitude.

On the other hand, there is no sharp distinction between colloidal and crystalloidal solutions, but as the particles in solution become smaller and smaller, the optical heterogeneity decreases correspondingly, finally vanishing as molecular dimensions are approached. That even crystalloid solutions are not in a strict sense homogeneous, is indicated by an experiment of van Calcar and Lobry de Bruyn (*Rec. Trav. chim. Pays-Bas*, 1904, 23, 218), who caused the crystallization of a considerable part of saturated crystalloid solutions at the periphery of a rapidly rotating centrifuge.\*

In an article entitled "Pedetic Motion in Relation to Colloidal Solutions" published in *Chemical News*, 1892, 65, 90, William Ramsay, Ph.D., F.R.S. (afterward Sir William Ramsay), clearly expressed this view in the following words: "I am disposed to conclude that solution is nothing but subdivision and admixture, owing to attractions between solvent and dissolved substance accompanied by pedetic motion; that the true osmotic pressure has, probably, never been measured; and that a continuous passage can be traced between visible particles in suspension and matter in solution; that, in the words of the old adage, *Natura nihil fit per saltum*."

#### SUBATOMIC PHYSICS

R. A. Millikan (Nobel Laureate, Cal. Insti. of Tech., see his book, "The Electron," also Alexander's "Colloid Chemistry,"

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\* See page 139 for recent work with ultracentrifuges.



Vol. I) has proved that what we call an "electric current" consists of a stream of particulate units carrying a negative charge (called *negative electrons*). Their number is so great, that Millikan estimates that if we were to set two and one-half million people to work counting the electrons which pass in *a single second* as an electric current through an ordinary incandescent bulb, and they were to count steadily at the rate of two per second, day and night, without stopping for any cause whatever, it would take them 20,000 years to accomplish the task. Furthermore, it has been shown that light is given out in little puffs, pulses, or *quanta* (Planck's quantum theory), this being due to the jets of energy given off by "excited" planetary electrons in atoms, when the electrons jump from some exterior "quantum position" to one further in (Bohr—Sommerfeld).

It would seem, therefore, that nature does many, if not most things, by leaps, only they are such tiny or rapid leaps, that they elude ordinary observation. For example, it would take  $10^{10}$  (that is, ten thousand million million) of the quanta of yellow sodium light to raise the temperature of one milligram of water one degree. (N. V. Sidgwick, Nobel Laureate, Oxford University).

The stuttering way in which many changes proceed is illustrated by the so-called "*chain-reactions*," in which activated units (see p. 10) are continuously and rapidly regenerated. Thus a mixture of chlorine and hydrogen gases, stable at ordinary temperatures, explodes violently on exposure to sunlight. The light is believed to form activated chlorine atoms from chlorine molecules:  $\text{Cl}_2 = \text{Cl}^\cdot + \text{Cl}^\cdot$ . The activated chlorine atoms unite with hydrogen molecules, setting free activated hydrogen:  $\text{H}_2 + \text{Cl}^\cdot = \text{HCl} + \text{H}^\cdot$ . The activated hydrogen atom can now regenerate an activated chlorine atom by reaction with a chlorine molecule:  $\text{Cl}_2 + \text{H}^\cdot = \text{HCl} + \text{Cl}^\cdot$ .

The recently evolved "wave mechanics" of L. de Broglie, Schrödinger, Heisenberg (Nobel Laureates) and others aim to explain phenomena not amenable to older theories, *e.g.*, the *photoelectric effect*, which is that electrons knocked out of certain metal surfaces have an energy dependent only on the *wave-length* of the light, not on its *intensity*. In epitome it may be said that radiant energy includes two factors—material corpuscles and a

wave system with a maximum crest. Considered as a *vibration* the energy of the photon (particle of light) is the frequency of vibration ( $\nu$ ) times Planck's constant ( $h$ ), while considered as a *mass* it is  $mc^2$  ( $c$  being the velocity of light in vacuo); that is,  $h\nu = mc^2$ . From this de Broglie deduces that the wave-length ( $\lambda$ ) associated with a mass  $m$ , moving with a velocity,  $v$ , equals Planck's  $h$ , divided by the particle's momentum; that is,  $\lambda = (h/mv)$ . Schrödinger introduces the concept of emission frequency as due to pulses or *beats* (in the acoustical sense) resulting from two or more vibrations coexisting in an atom. Special treatises must be consulted regarding these new developments, which may reconcile Newton's corpuscular theory with the light-wave theory of Young and Fresnel.

### CHEMISTRY AND THE NEW QUANTUM MECHANICS

The mathematical physicist and the physical chemist have been breaking down the purely pedagogic barriers which had been erected between physics and chemistry; and their development of a quantum or "electronic" mechanics is working in the sub-microscopic cosmos the same general type of basic revolution as did the discoveries of Kepler and Newton in the celestial field of mechanics. We must not forget, however, that Kepler's formulation was based on the pains-taking and laborious observations of Tycho Brae.

In order to give some inkling as to the importance and nature of this new field, the following is quoted from a paper by Prof. Henry Eyring (Princeton) in *The Scientific Monthly*, 1934, 39, 415-9:

"We now inquire what is the nature of this mechanics, which is transforming chemistry from a world in which every property of matter was of necessity empirical to one in which any property can be calculated—to be sure, at the price of enormous labor—but nevertheless it can be calculated. Since all the forces between atoms arise from the fact that they are electrical charges, it is not surprising that when we can specify accurately the average relative position of these charges we can immediately calculate all their properties. The *eigenfunction* is the name given to the quantity whose square describes in detail the haunts of these

particles, and the *Pauli principle* simply says that no two of these particles can simultaneously occupy the same haunts. . . . Now the other important principle in quantum mechanics tells us how, by a slight but absolutely definite change, we obtain an operator\* from the Newtonian expression for a property, which acts upon an eigenfunction to yield the corresponding value of this property in our new mechanics."

Chemical reaction between molecules results from a collision so violent that "the atoms in the two colliding molecules must approach so closely that they no longer know whether they are bound to the new or the old atoms. For convenience, this is known as *the activated state*. If these violent encounters occur once in every million million collisions, the reaction goes moderately fast. If they go once in every thousand million collisions, an experimental chemist will be unable to distinguish between this and reaction on every collision. He will simply say in either case that the reaction goes immeasurably fast." Quantum mechanics permits the calculation as to how energetic a collision must be to effect chemical change, and, therefore, at what temperature such change will proceed at a measurable rate, thus obviating long and expensive experiments. It also permits the definition of catalytic efficiency, and the calculations of how closely molecules approach in ordinary, non-reactive collisions, thus defining the "size" of molecules.

It must be remembered, however, that the relations dealt with by quantum mechanics underlie, but are in no way in conflict with, those other relations which emerge when molecules group together to form larger masses. If we divide any phenomenon into two factors (1) the physical or material units involved ( $M$ ), and (2) the behavior of those units ( $B$ ), the phenomenon ( $P$ ) is a function ( $f$ ) of both  $M$  and  $B$ , a fact which mathematicians express in a concise form, or *formula*, as follows:

$$P = f(M\bar{B})$$

Since  $M$  and  $B$  together must express the whole phenomenon, naturally the more basic and simpler the material units we decide

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\*In mathematics the term "operator" means a symbol that briefly indicates a mathematical process or a set of such processes, and that admits of analytical treatment.—J. A.

to use in our explanation, the more complicated will become the behavior factor, and also the mathematical equations expressing it. Theoretically, an elephant might be expressed in terms of atoms, even of electrons; but no human mind could conceive the equations, nor could anyone live long enough to read even part of them. Generally, we are prone to stick to relatively simple behavior factors and to allow most of the complexities of a phenomenon to accumulate innocuously in the material units. When driving an automobile, we think of the car as a unit, and, when necessary, of the various dials, levers, and pedals controlling the mechanism. The intricate mechanical details of construction and operation, and the much more intricate molecular, atomic, and electronic facts, are completely submerged. We could not begin to understand or to operate the car in terms of atoms or electrons, even though the car is composed of them.

Furthermore, there are good philosophical reasons for refusing to accept, without experimental confirmation, calculations as to the behavior of larger masses or structures, based upon what we know of the behavior of smaller units, or structures. This view has been succinctly stated by Prof. Percy W. Bridgman (Harvard) on the occasion of his acceptance of the Comstock Prize of the National Academy of Sciences ("Science", 1933, 78, 504):

"There are two very broad purposes which may be furthered by a study of large-scale phenomena, which in principle cannot be obtained from small-scale phenomena. In the first place, modern theoretical physics seems committed to the thesis that all large-scale phenomena can be completely understood in terms of the properties of the small-scale elements. A justification for this can be only empirical, and that justification has not yet been given by any means. It is entirely conceivable that large-scale matter might embody properties which biologists would call 'emergent', which cannot be predicted from even an exhaustive knowledge of the properties of the isolated elements. We can never be sure of the thesis that there are no 'emergent' properties until the explanation of large-scale properties is completely worked out, and for this reason it is important that our knowledge of large-scale properties be as wide as possible. In the second place, the concepts in terms of which we describe small-scale ex-

perience are themselves derived from large-scale experience, and it is therefore vital that the concepts be adequate to describe the large-scale experience. These concepts were a slow growth and the result of long rumination, continual fitting and adjustment, to insure that the evolving concepts completely corresponded to all the known experimental facts. The later generations forget this slow process of growth, and accept the concepts as they find them. But the discovery of new experimental facts beyond the range of those known when the concept was crystallized should demand a reexamination of the concept to determine whether it is still adequate. Only by being everlastingly self-conscious of the experimental basis of our concepts and the possibility of necessary revision as knowledge of large-scale phenomena broadens, can we be sure that the basis for our theoretical speculations remains sound."

## CHAPTER II

### MATERIAL UNITS AND THE FORCES DOMINATING THEM

THERE are many perfectly sane, capable, and earnest people who have not been trained to follow, or who cannot follow mathematical reasoning, even when all the successive steps are given in painful detail—which good mathematicians seldom do, since they assume the reader possesses a good mathematical background. Thus in one of his treatises, J. Clerk Maxwell, after establishing a certain equation said: “By inspection, we see that”—and then he jumped to another equation. The writer, then a student, worked a full hour before he discovered how the second equation was derived from the first. We can therefore appreciate the English school-boy’s description of algebra as “a low form of cunning.”

However, it is encouraging to know that we can enjoy the beauty of a cathedral without understanding all the details of the scaffolding by aid of which the structure was built, although most people will readily grasp the general principles involved in the scaffolding, provided they are not stunned by details. Simple mathematics is simple reasoning. Thus most people will agree that  $2 + 2 = 4$ , although in certain financial circles they say  $2 + 2 = 22$ . Complicated mathematics involves complicated reasoning, or, what amounts to the same thing, conducting simultaneously many simple lines of reasoning—which many persons find confusing.\*

But even skilful mathematicians may run into trouble when they attempt to apply mathematics to the solution of natural phenomena. Take the simple case of the greyhound running at 600 yards per minute<sup>‡</sup>, chasing the rabbit running at 500 yards per minute, that is 100 yards per minute slower than the grey-

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\* A rat which cleverly avoided each trap that was set for him, was caught when *two* traps were set.

hound. If the rabbit has a head start of 100 yards, the greyhound should overtake him in just one minute. However, if we remove this problem from the desk to the field, and actually set a real greyhound after a real rabbit, surprising things are apt to happen. Thus, before being caught, the rabbit may pop into his hole. Or a hawk may swoop down and snatch him off before the greyhound gets him. Or a barbed wire fence may let the rabbit pass but hold up the greyhound. Or the greyhound might run a thorn into his foot and lose speed or even stop altogether.

The disgusted mathematician will tell you that all this is not in the problem. Of course not—but it may occur in nature. Really, in framing a statement about a problem, whether we put it into the form of a mathematical equation or not, we make the following basic assumptions: *First*, that what we *do* say corresponds to the actual facts; *Second*, that we have included *every* factor exerting an effect. The first may be carefully safeguarded; where we get into trouble it is generally because there are factors we do not think of, know of, or even imagine as existing. Nature is so full of unexpected or unthought of influences, that we must add to our conclusions what the certified public accountant adds to his report—E. and O. E. (errors and omissions excepted).

Next to accurate observation and due allowance for all influential factors involved, perhaps nothing is more important in scientific matters than the mental separation of seasoned facts from the theories designed to systematize and explain them. For facts are hard, stubborn things that survive the theories whose downfall they may cause.

A theory must interminably run the gauntlet of the whole far-flung tribe of scientists, and may be stricken down after long years of apparent safety. Einstein's Theory of Relativity has been checked by astronomers and physicists in such diverse fields as the deflection of alpha particles shot out from radium, the deviation of starlight by the sun, and the precession of the axis of the orbit of the planet Mercury. How convenient it would be if a scientist, when confronted with facts that run counter to the very theories he has been taught to revere, could only say, as Ko-Ko remarked to Pooh-Bah:—"Come over here where the Lord High Treasurer can't hear us!"

TABLE I—STABLE ATOMIC SPECIES\*

(Numbers in italics are rough or indirect measurements, in parentheses doubtful.)

Symbol	Atomic Number (Z)	Isotopic Number	Mass Number (M)	Relative Abundance (%)
n	0	1	1	(100)
H	1	—1	1	99.98
D		0	2	0.02
T		1	3	$7 \times 10^{-8}$
He	2	0	4	100
Li	3	1	6	7.9
			7	92.1
Be	4	0	(8)	(0.05)
		1	9	99.95
B	5	0	10	20
		1	11	80
C	6	0	12	99.3
		1	13	0.7
N	7	0	14	99.62
		1	15	0.38
O	8	0	16	99.76
		1	17	0.04
		2	18	0.20
F	9	1	19	100
Ne	10	0	20	90.00
		1	21	0.27
		2	22	9.73
Na	11	1	23	100
Mg	12	0	24	77.4
		1	25	11.5
		2	26	11.1
Al	13	1	27	100
Si	14	0	28	89.6
		1	29	6.2
		2	30	4.2
P	15	1	31	100
S	16	0	32	96
		1	33	1
		2	34	3

\* The author thanks Prof. Wm. D. Harkins (Univ. of Chicago) and Prof. F. W. Aston (Cambridge University) for information supplied. D is deuterium (heavy hydrogen), while T is the much rarer tritium (triple hydrogen). Bonhoeffer, Harteck and Eucken have shown that the molecule of ordinary hydrogen ( $H_2$ ) exists in two forms, determined by nuclear spin and termed ortho- and parahydrogen (see "Orthohydrogen, Parahydrogen, and Heavy Hydrogen," by A. Farkas, Cambridge Univ. Press, 1935.)



TABLE I—STABLE ATOMIC SPECIES (*Continued*)

(Numbers in italics are rough or indirect measurements, in parentheses doubtful.)

Symbol	Atomic Number (Z)	Isotopic Number	Mass Number (M)	Relative Abundance (%)
Cl	17	1	35	76
		3	36	24
A	18	0	36	0.33
		2	38	0.05
		4	40	99.62
K	19	1	39	93.3
		3	41	6.7
			40	$K^{40} = \frac{1}{8500} K^{39}$
Ca	20	0	40	96.76
		2	42	0.77
		3	43	0.17
		4	44	2.30
Sc	21	3	45	100
Ti	22	2	46	8.5
		3	47	7.8
		4	48	78.3
		5	49	5.5
		6	50	6.9
V	23	5	51	100
Cr	24	2	50	4.9
		4	52	81.6
		5	53	10.4
		6	54	3.1
Mn	25	5	55	100
Fe	26	2	54	6.5
		4	56	90.7
		5	57	2.8
		6	58	
Co	27	5	59	100
Ni	28	2	58	67.5
		4	60	27.0
		6	62	3.8
		8	64	
Cu	29	5	63	68
		7	65	32

TABLE I—STABLE ATOMIC SPECIES (*Continued*)

(Numbers in italics are rough or indirect measurements; in parentheses doubtful.)

Symbol	Atomic Number (Z)	Isotopic Number	Mass Number (M)	Relative Abundance (%)
Zn	30	4	64	50.4
		6	66	27.2
		7	67	4.2
		8	68	17.8
		10	70	0.4
Ga	31	7	69	61.5
		9	71	38.5
Ge	32	6	70	21.2
		8	72	27.3
		9	73	7.9
		10	74	37.1
		12	76	6.5
As	33	9	75	100
Se	34	6	74	0.9
		8	76	9.5
		9	77	8.3
		10	78	24.0
		12	80	48.0
		14	82	9.3
Br	35	9	79	50
		11	81	50
Kr	36	6	78	0.42
		8	80	2.45
		10	82	11.79
		11	83	11.79
		12	84	56.85
		14	86	16.70
Rb	37	11	85	72
		13	87	28
Sr	38	10	86	10.0
		11	87	6.6
		12	88	83.4
Y	39	11	89	100
Zr	40	10	90	48
		11	91	11.5
		12	92	22
		14	94	17
		16	96	1.5

TABLE I—STABLE ATOMIC SPECIES (*Continued*)

(Numbers in italics are rough or indirect measurements, in parentheses doubtful.)

Symbol	Atomic Number (Z)	Isotopic Number	Mass Number (M)	Relative Abundance (%)
Nb	41	11	93	100
Mo	42	8	92	14.2
		10	94	10.0
		11	95	15.5
		12	96	17.8
		13	97	9.6
		14	98	23.0
Ru	44	16	100	9.8
		8	96	5
		10	98	?
		11	99	<i>12</i>
		12	100	<i>14</i>
		13	101	<i>22</i>
Rh	45	14	102	<i>30</i>
		16	104	17
Rh	45	13	103	100
Pd	46	10	102	
		12	104	
		13	105	
		14	106	
		16	108	
		18	110	
Ag	47	13	107	52.5
		15	109	47.5
Cd	48	10	106	1.51
		12	108	1.01
		14	110	15.32
		15	111	15.32
		16	112	21.98
		17	113	15.02
		18	114	23.89
		20	116	5.95
In	49	15	113	4.5
		17	115	95.5
Sn	50	12	112	1.10
		14	114	0.76
		15	115	0.45
		16	116	14.63
		17	117	10.11
		18	118	22.14
		19	119	11.36

TABLE I—STABLE ATOMIC SPECIES (*Continued*)

(Numbers in italics are rough or indirect measurements, in parentheses doubtful.)

Symbol	Atomic Number (Z)	Isotopic Number	Mass Number (M)	Relative Abundance (%)
		20	120	27.88
		22	122	5.19
		24	124	6.38
Sb	51	19	121	56
		21	123	44
Te	52	18	122	2.9
		19	123	1.6
		20	124	4.5
		21	125	6.0
		22	126	19.0
		24	128	32.8
		25	129	33.1
I	53	21	127	100
Xe	54	16	124	0.08
		18	126	0.08
		20	128	2.30
		21	129	27.13
		22	130	4.18
		23	131	20.67
		24	132	26.45
		26	134	10.31
		28	136	8.79
Cs	55	23	133	100
Ba	56	23	135	5.9
		24	136	8.9
		25	137	11.1
		26	138	74.1
La	57	25	139	100
Ce	58	24	140	89
		26	142	11
Pr	59	23	141	100
Nd	60	22	142	36
		23	143	11
		24	144	30
		25	145	5
		26	146	18
Sm	62	20	144	3
		23	147	17

TABLE I—STABLE ATOMIC SPECIES (*Continued*)

(Numbers in italics are rough or indirect measurements, in parentheses doubtful.)

Symbol	Atomic Number ( <i>Z</i> )	Isotopic Number	Mass Number ( <i>M</i> )	Relative Abundance (%)
		24	148	14
		25	149	15
		26	150	5
		28	152	26
		30	154	20
Eu	63	25	151	50.6
		27	153	49.4
Gd	64	27	155	21
		28	156	23
		29	157	17
		30	158	23
		32	160	16
Tb	65	29	159	100
Dy	66	29	161	22
		30	162	25
		31	163	25
		32	164	28
Ho	67	31	165	100
Er	68	30	166	36
		31	167	24
		32	168	30
		34	170	10
Tm	69	31	169	100
Yb	70	31	171	9
		32	172	24
		33	173	17
		34	174	38
		36	176	12
Lu	71	33	175	100
Hf	72	32	176	5
		33	177	19
		34	178	28
		35	179	18
		36	180	30
Ta	73	35	181	100
W	74	34	182	22.6
		35	183	17.3

TABLE I—STABLE ATOMIC SPECIES (*Continued*)

(Numbers in italics are rough or indirect measurements, in parentheses doubtful.)

Symbol	Atomic Number (Z)	Isotopic Number	Mass Number (M)	Relative Abundance (%)
Re	75	36	184	30.2
		38	186	29.9
		35	185	38.2
		37	187	61.8
Os	76	34	186	1.0
		35	187	0.6
		36	188	13.4
		37	189	17.4
		38	190	25.1
		40	192	42.5
Ir	77	37	191	
		39	193	
Pt	78	36	192	
		38	194	
		39	195	
		40	196	
		42	198	
Au	79	39	197	100
Hg	80	36	196	0.10
		38	198	9.89
		39	199	16.45
		40	200	23.77
		41	201	13.67
		42	202	29.27
		43	203	0.006
		44	204	6.85
Tl	81	41	203	29.4
		43	205	70.6
Pb	82	39	203	0.04
		40	204	1.51
		41	205	0.03
		42	206	27.99
		43	207	20.37
		44	208	49.98
		46	210	0.08
Bi	83	43	209	100
Th	90	52	232	(100)
U	92	51	235	
		54	238	(100)

## DIVISIBILITY OF SO-CALLED ELEMENTS

Among the disconcerting discoveries of recent times may be mentioned those connected with radio-activity, which eventually led to the demonstration that electricity consists of discrete particles, and that our supposedly infrangible elements are complexes of subatomic particles, and that some of these complexes are breaking up spontaneously and uncontrollably, while others may be shattered by the terrific impact of alpha particles moving at the rate of 10,000 miles or more per second.

Then the basic assumption of Dalton's atomic theory fell, when T. W. Richards, J. J. Thompson, Aston, Dempster, Harkins and others showed that with many of the elements, the atoms are not all alike, but have different atomic weights. In an address before the British Association for the Advancement of Science, Dr. F. W. Aston (Cambridge University) stated: "In artificial radioactivity and transmutation we see the real beginning of a new great subject, the nuclear chemistry of the future. Its equations can only be founded securely upon direct determinations of masses by the mass-spectrograph, and the nuclear chemist already demands these to an accuracy of 1 in 100,000. . . . Armed with reliable equations, and thereby with more and more knowledge of nuclear construction, he will transmute and synthesize atoms as his elder brother has done molecules, with results to be wondered at and possibly even misused by his fellow creatures. I foresee a time, not immeasurably far distant, when it will be possible for us to synthesize any element whatever, wherever, and whenever we please, alchemy indeed in the service of man." ("Science," 1935, 82, 235-240).

It is startling to learn, for example, that lithium consists of a mixture of atoms having atomic weights of 6 and 7, chlorine of atoms having atomic weights of 35 and 37, and that tin has eleven *isotopes*, as they are called. In an address before the Chemical Society (London) Aston remarked:—"Though as a chemist I view with some dismay the possibility of eighteen\* different mercuric chlorides, as a physicist it is a great relief to find that nature employs at least approximately standard bricks in her

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\* Since this was written (about 1928) mercury has been found to have eight isotopes, which with the two isotopes of chlorine, give 24 different kinds of mercuric chloride.

operations of element building." And, to the endless disgust of small boys, Harkins has pointed out the possibility of 63 different kinds of calomel, now increased to 108 because of newly recognized isotopes of mercury.

Some of our other new discoveries cast doubt upon what were heretofore accepted as facts. Thus the recognition of vitamins and certain salts as food essentials has necessitated the re-examination of conclusions drawn from some previous experiments on food values, which in some cases showed simply the minimum quantities of food needed to supply the necessary amount of vitamins or salts. The incompleteness of mere calorie-fat-protein-carbohydrate specifications for food is now well recognized.

The kind of protein is important, for the body demands certain kinds of amino acids. Gelatin, though an excellent food, lacks tyrosine and tryptophane, and must be supplemented by other proteins. Proteins having closed rings or aromatic structure may serve as "raw material" for making minute but essential amounts of hormones. Jordan-Lloyd ("Chemistry of the Proteins," 1926) suggested tyrosine as a precursor of adrenaline.

### CHEMICAL VS. PHYSICAL FORCES\*

We make free use of the expressions "physical mixture" and "chemical compound" with the full confidence that we know exactly what we are talking about. But when we attempt to define these terms exactly, we appreciate the truth of Aristotle's remark that to frame an exact definition requires complete knowledge.

In writing the formula for a double salt, *e.g.*  $\text{PtCl}_4 \cdot 2 \text{KCl}$ , as used to be the custom, Professor Ira Remsen (John Hopkins University) would point to the period in the formula, and remark with a twinkle in his eye: "That period has for many years been a full stop to thought. Don't let such devices keep you from trying to find out what lies behind them."

The difference between chemical and physical attraction is explained in many elementary text books by taking the example of iron filings and flowers of sulphur. From their physical mix-

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\* Interesting in this connection is the introductory lecture of Prof. N. V. Sidgwick (Oxford University) at Cornell University. See "Science," 1931, 73, 269-76.



ture the iron may be separated magnetically or the sulphur dissolved out by carbon bisulphide; and the two ingredients may be separately identified in the microscope. If they are heated, however, the non-magnetic chemical compound FeS is formed, from which CS<sub>2</sub> extracts no S. Furthermore, while Fe and S may be physically mixed in any desired proportions, in the chemical compound FeS they combine in the definite proportions of 56 parts by weight of Fe to 32 parts by weight of S, and any excess of S may be dissolved out by CS<sub>2</sub>.

This fixes homogeneity and closeness of union in definite proportions by weight, as criteria of chemical combination.

But the transition between chemical and physical forces is not so sharp as our definitions demand; and it is in the transition zone that there appear the phenomena encountered in that extremely fine state of subdivision or dispersion known as the colloidal condition, where combination depends *not* upon the *total mass* involved, but upon the *total free or active surface*.

The so-called "*order*" of a chemical reaction is the number of molecules which determine its velocity (Prof. J. H. Hildebrand, University of California, "Principles of Chemistry," p. 148). Thus, for example,

A reaction of the first order:  $\text{CaCO}_3 = \text{CaO} + \text{CO}_2$

A reaction of the second order:  $\text{H}_2 + \text{Cl}_2 = 2 \text{HCl}$

A reaction of the third order:  $2 \text{FeCl}_3 + \text{SnCl}_2 = 2 \text{FeCl}_2 + \text{SnCl}_4$

The reaction  $2 \text{C}_2\text{H}_2 + 5 \text{O} = 4 \text{CO}_2 + 2 \text{H}_2\text{O}$  appears to depend upon the meeting of seven molecules and to be of the seventh order. It is evident, however, that there are intermediate or subsidiary reactions—a slow one determinative of the rate of the whole reaction, which probably is  $\text{C}_2\text{H}_2 + 2 \text{O} = 2 \text{CO} + \text{H}_2$ , followed by two much more rapid ones,  $2 \text{CO} + \text{O}_2 = 2 \text{CO}_2$ , and  $2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O}$ .

### DO COLLOIDS FORM CHEMICAL COMBINATIONS?

The answer depends upon what is meant by "chemical combination." It is generally understood to mean combination in fixed, definite proportions, resulting from precise union of atoms, radicals or molecules. Now suppose that a real definite chemical

compound were formed at some edge or corner of a large molecular mass of indefinite size—would it be fair to call the whole huge mass a chemical compound? If we spill a drop of nitric acid on our sleeve, do we thereby make nitrate of coat? If we stick a postage stamp on a letter, do we thereby make stampate of envelope or envelopate of stamp? Sodom and Gomorrah might have been saved by the presence of ten good men; but even a larger number of definite molecules cannot entitle a huge cluster to the saving grace of a chemical name. It is hardly fair to distort the accepted meaning of the term "chemical compound," because nature permits molecules to have many and strong residual attractions. After all, we must accept Nature as she is, and not try to force her into a stoichiometric straight-jacket.

Pointing out that Gay-Lussac and Avogadro recognized the existence of indefinite compounds, J. M. van Bemmelen stated (Rec. trav. chim. Pays-Bas, 1888, 7, 37; "The Foundations of Colloid Chemistry," E. Benn Ltd., 1925, p. 121):

"It seems to me that one does not in general sufficiently distinguish the colloidal combinations of oxides or of salts with water from true hydrates. The former are indefinite bodies of indefinite composition, the latter true chemical compounds. In the textbooks of chemistry, and also in many recent researches, these compounds of indefinite composition appear with chemical formulae, as if there were simple ratios between their constituent atoms or molecules, and as if they belonged to the class of ordinary chemical compounds. This also applies to a large class of bodies which might be called *absorption compounds*. They are met with particularly when colloidal substances are treated with solutions of an acid, a base, a salt, etc."

Since definite chemical compounds represent temporary minima of potential for the conditions under which the compounds are stable, atoms naturally try to reach this minimum, and do so unless something intervenes. But there is many a slip between the atomic cup and lip. Competing ions, atoms, molecules, or larger masses often secure coigns of vantage from which they are not readily ousted, if at all, by other units seeking to form precise chemical compounds. Even when chemical compounds attempt to form the perfect space lattice of a clean crystal,

stranger particles shoulder their way in and remain, though in most cases they may be eliminated by repeated crystallization.

There is a difference of opinion as to whether *water of crystallization* is bound chemically or physically. True, it is fixed in stoichiometric proportions; but it is so readily taken up, changed, or removed, that it is generally regarded as physically bound. Thus the common form of sodium sulphate is Glauber's salt,  $\text{Na}_2\text{SO}_4 \cdot 10 \text{H}_2\text{O}$ ; but if a boiling saturated solution is allowed to cool in a closed vessel, unstable oblique rhombic prisms of  $\text{Na}_2\text{SO}_4 \cdot 7 \text{H}_2\text{O}$  appear when the temperature drops to  $17.9^\circ \text{C}$ . If the solution is slowly heated, after saturation at  $33^\circ \text{C}$ ., the sulphate deposits as anhydrous rhombic octahedra. Some crystals (Glauber's salt, and  $\text{Na}_2\text{CO}_3 \cdot 10 \text{H}_2\text{O}$ ) give up water to the atmosphere, *i.e.*, are *efflorescent*. Others take water from the air ( $\text{K}_2\text{CO}_3$  and  $\text{CaCl}_2$ ), *i.e.* are *deliquescent*. Alum crystals ( $\text{Al K}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ ) when heated to gradually increasing temperatures, lose water progressively—10 parts at  $100^\circ \text{C}$ ., 10 parts at  $120^\circ \text{C}$ ., and the balance at  $200^\circ \text{C}$ . Alum first melts in its own water of crystallization, and then froths into a tenacious pastey mass (*intumescence*). Though copper sulphate crystallizes as  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$  (blue vitriol or bluestone), if much ferrous sulphate is also present the copper sulphate forms with it crystals isomorphous with the iron salt, having 7  $\text{H}_2\text{O}$ . P. P. von Weimarn and his pupils have shown (see Alexander's "Colloid Chemistry, Theoretical and Applied," Vol. I, p. 647), by merely grinding crystals having water of crystallization, that this acts just like adsorbed water.

Wherever a colloidal dispersion consists of subsidiary units striving toward a position of lower potential, the dispersion is in *metastable* condition. On ageing, it will tend to reach the lower potential level, and will have a "life", which may, however, be a very long one. Colloidal silica is found in nature; and aragonite, the metastable form of calcium carbonate, has persisted for ages without transforming into calcite, the stable form.

Since the criterion of colloidity is particulate dimension (particle size), a colloidal particle may consist of one single molecule of a definite chemical compound, providing only that the molecule is big enough. Such a chemical compound would

form a colloidal solution when molecularly dispersed, even though it might, under suitable conditions be made to yield perfect crystals. On the other hand, if a colloidal particle consists of an aggregation of atoms or molecules, these may be grouped in amorphous, haphazard or random fashion; or they may be assembled so as to form tiny *colloidal crystals* as is the case with colloidal gold. *Amorphous and crystalline colloidal particles* may co-exist in the same sol of silicic acid, as Scherrer found by X-ray examination.

### THE SUBMICROSCOPIC STRUCTURE OF MATTER

A whole series of complexities underlie even the smallest particle of matter visible in the most powerful microscope. While the number of steps in this series may vary in individual cases, in many instances the degrees of aggregation shown in Table II may be definitely traced.

Some idea as to the immensity of space and the distribution of matter in it, is given by Dr. Edwin Hubble of the Mt. Wilson Observatory of the Carnegie Institution (Scientific Monthly, Sept., 1934). He compares our stellar system to a drifting swarm of bees, our sun, with its relatively insignificant family of planets, being a fairly small star in the swarm. Astronomers, peering out into the vast emptiness of space, see other stellar systems so distant that they appear merely as unresolvable patches of light, and are called *nebulae* (*i.e.*, clouds). The faintest nebulae detectable with our present telescopes, lie at the surface of a sphere roughly 600 million light years in diameter (the "observable region"), within which are scattered about 100 million nebulae, averaging one and a half million light years apart, 80 million times brighter than the sun, and 800 million times greater in mass than the sun. Whatever matter may be scattered between the nebulae is insufficient in amount appreciably to dim the most distant ones we can see; and omitting this from consideration, the concentration of matter in the visible region figures out to about one gram per  $10^{30}$  cubic centimeters, which is equivalent to one grain of sand in each volume of space equal to that of the earth.



TABLE II (Continued)

				Biological Units
Molecules				Micromolecule #
Molecular groups		0.2-5 $m\mu$	Ultramicroscopic limits—about 2 $m\mu$ .	
		0.5-10 $m\mu$	Amplitude of Brownian motion } of Pt hydrosol at 19° C. Av. } particle size = 25 $m\mu$	
Primary colloidal particles		2-20 $m\mu$	Connecting zone between shortest ultraviolet and longest X-rays 60-8 $m\mu$ .	20 - 70 $m\mu$ —Genes
Secondary colloidal particles		5-100 $m\mu$	$\left\{ \begin{array}{l} \text{CO}_2 = 61.5 \text{ } m\mu \\ \text{NH}_3 = 66.0 \\ \text{N} = 92.9 \\ \text{O} = 99.3 \\ \text{H} = 160.0 \\ \text{He} = 300.0 \end{array} \right.$ Visible spectrum Microscopic limits for resolution about 250 $m\mu$ .	50 $\pm$ $m\mu$ —Bacteriophage
Microscopically resolvable particles		Over 100 $m\mu$	$\left\{ \begin{array}{l} \text{Violet—about 4,000 \AA. (400 } m\mu) \\ \text{Blue—4,700 \AA.} \\ \text{Green—5,200 \AA.} \\ \text{Yellow—5,800 \AA.} \\ \text{Orange—6,000 \AA.} \\ \text{Red—6,500 \AA.} \end{array} \right.$ Limits of visibility—	2 $\pm$ $\mu$ = Cocci (round bacteria) 0.2 - 3.5 $\mu$ —Chromosome 5 $\mu$ - 15 $\mu$ —Cell nuclei
Visible particles		Over 50 $\mu$	Longest infra red from Hg vapor—0.313 mm. (313,000 $m\mu$ ). Shortest Hertzian waves 2.0 mm. (2,000,000 $m\mu$ ). † Electro-magnetic vibrations of alcohol—70.0 cm. Hertzian wireless waves 100 m.—30,000 m.	7 $\mu$ - 25 $\mu$ —Cell 2.5 mm. <i>Drosophila melanogaster</i> (the "fruit fly"). §

$N$ —number of molecules in 1 gram molecule =  $60.62 \times 10^{23}$ .  
 $h$ —Planck's constant of action  $655 \times 10^{27}$  erg seconds.  
 $e$ —charge of the electron  $4.774 \times 10^{-10}$  electrostatic units.  
 Human voice 60—12,000 vibrations per second. (human).  
 Audible sound 16—30,000 " " (mice).  
 Mechanically detectable 60,000  $\pm$  " " (Koenig).  
 90,000 " " "

\* Lorentz, from electromagnetic theory.

† Rutherford's estimate from experiment.

‡ Nichols and Tear.

§ The estimates for the sizes of the cell, cell nucleus, chromosomes and genes apply to *Drosophila melanogaster*

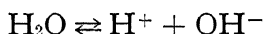
The weight of matter in the Einsteinian universe is estimated to be  $8 \times 10^{78}$  grams. F. W. Aston (*Nature*, 1924, 113, 393) estimates the weight of the solids of the earth (*the lithosphere*) to be  $5.98 \times 10^{27}$  grams; the water or *hydrosphere*,  $1.45 \times 10^{24}$  grams; and the *atmosphere*,  $5.29 \times 10^{21}$  grams.

Taking Harlow Shapley's estimate of the diameter of the galaxy of 300,000 light years = approximately  $2.5 \times 10^{21}$  cm., we see that in an *exponential* range of 37\* we may pass from the smallest known material unit, the proton, to the outermost confines of the Milky Way. This indicates the extent of the variations in real values represented by the pH *exponential* figures so often used to express the effective acidity or alkalinity of colloidal solutions. When using Sørensen's convenient pH symbolism we must remember that it is an *inverse exponential function*.

### HYDROGEN ION CONCENTRATION

The expression pH demands some explanation.† It is a convenient way to express the reaction of any fluid, but is dangerous because it does not do this directly; for it is an inverse logarithmic function, deprived of its minus sign, as will be seen directly.

Pure water dissociates slightly according to the equation



the reaction being reversible. It has been found that at 22° C. the concentration of hydrogen ions in pure water equals

$\frac{1}{10,000,000}$  moles per liter, a fact usually expressed by the symbolism  $C_{\text{H}^+}$  (concentration of hydrogen ions) equals  $10^{-7}$  moles per liter. Since for each  $\text{H}^+$  ion in water there is an  $\text{OH}^-$  ion,  $C_{\text{OH}^-} = 10^{-7}$  under the same conditions.

Now, for convenience, Sørensen proposed to disregard the minus sign, and to use simply the numerical value of the exponent of 10 to express the reaction represented by the corresponding  $C_{\text{H}^+}$ . Table III ‡ will make this clear:

\* That is, the proton has a diameter of the order of  $10^{-10}$  cm. and the galaxy a diameter of the order of  $10^{21}$  cm., the exponential spread being 37.

† It was derived from *pouvoir* hydrogène (the exponent or power of hydrogen).

‡ "Die Wasserstoffionen Concentration," by Prof. Leonor Michaelis.

TABLE III

	Degree of normality	$\text{CH}^+$	Equivalent pH value
HCl	1.0	$8.0 \times 10^{-1}$	0.10
	0.1	$8.4 \times 10^{-2}$	1.07
	0.01	$9.5 \times 10^{-3}$	2.02
	0.001	$9.7 \times 10^{-4}$	3.01
	0.0001	$9.8 \times 10^{-5}$	4.01
Acetic acid	1.0	$4.3 \times 10^{-3}$	2.37
	0.1	$1.6 \times 10^{-3}$	2.87
	0.01	$4.3 \times 10^{-4}$	3.37
	0.001	$1.6 \times 10^{-4}$	3.87
Caustic soda	1.0	$0.90 \times 10^{-14}$	14.05
	0.1	$0.86 \times 10^{-13}$	13.07
	0.01	$0.76 \times 10^{-12}$	12.12
	0.001	$0.74 \times 10^{-11}$	11.13

This table shows that the lower the pH value, the greater the *ionizable* or *effective reaction* of acidity, which is something quite different from the *titratable* or *total* acidity. Thus equal volumes of normal hydrochloric acid and of normal acetic acid will neutralize equivalent volumes of normal alkali, but the normal acetic acid has a much lower degree of ionized acidity or hydrogen ion concentration, and therefore a higher pH value.

Not only does the pH value run *opposite* the H ion concentration, but the variations are exponential or logarithmic, not arithmetical. The step between pH 5 and pH 6 is vastly less than the step between pH 5 and pH 4, as may be seen from the following table:

pH value	Number of times H (or OH) ion concentration exceeds that of pure water	
1	1,000,000	
2	100,000	
3	10,000	
4	1,000	
5	100	acid side
6	10	
7	0	pure water
8	10	
9	100	alkaline side
10	1,000	
11	10,000	
12	100,000	
13	1,000,000	



*Buffer Action* is the ability of a solution, sol, or gel, to withstand successfully factors which would tend to change its pH value. Buffer substances are able to combine with or adsorb small amounts of added H or OH ions; as examples may be mentioned phosphates, borates, proteins. Pure water is entirely unbuffered, and its pH is quickly changed by almost anything with which it comes into contact. Thus the pH of ordinary distilled water varies from about 5.5 to 6.5 depending on the kind of still used and the extent of its exposure to absorption of atmospheric carbon dioxide.

But an acid can neutralize a base in benzene solution, where there is no H/OH dissociation, as in water. Prof. T. M. Lowry and Prof. J. N. Brønsted independently suggested that the classical earlier theory be extended, so that an acid may be defined by what it does physically, irrespective of what happens to the solvent. Accordingly, an acid is a donor, or source of protons; and a base is an acceptor of protons, *i.e.*, a substance that can combine with protons. A proton, naturally, is a naked nucleus,  $H^+$ , of ordinary hydrogen (protium); but the nuclei of deuterium and of tritium may act similarly. This newer view isolates the acid/base equilibrium from the changes suffered by any solvent, and makes for a more general theory. Further discussion of this view will be found in recent books on physical chemistry, *e.g.*, that of Dr. S. Glasstone (Blakiston, 1933). It indicates that water is amphoteric, *i.e.*, it may act as an acid or as a base depending on conditions.

### HOMOGENEITY AND HETEROGENEITY—PHASES

Lewis and Randall ("Thermodynamics," p. 9) describe a *homogeneous system* as one in which there are no apparent surfaces of discontinuity; and a *heterogeneous system* as one consisting of two or more distinct homogeneous regions or *phases*, which appear to be separated from each other by surfaces of discontinuity. The celebrated Phase Rule of J. Willard Gibbs [Trans. Conn. Acad. Sci., 1876, 3, 228] is that the number of *degrees of freedom* ( $F$ ) of a system as a whole (in other words the number of independent variables upon which it depends) equals the number of variables essential to determine the state of the individual phases, minus the sum of the phases outside the first.

Thus in a system of  $n$  phases whose individual states are controlled by  $x$  variables,

$$F = x - (n - 1) = x - n + 1$$

But as Zsigmondy pointed out ("Colloids and the Ultramicroscope," p. 3) and as the table (p. 28) showing the serial complexity of matter indicates, the practical distinction between homogeneity and heterogeneity depends entirely upon the refinement of our means of observation. In many cases we assume phases to be homogeneous to simplify our calculations; but when a substance is finely subdivided or dispersed, the influence of specific surface (exterior or rind surface) becomes an important factor, the phases neglected or submerged for our convenience urgently demand consideration, and the number  $n$  in Gibbs' equation must be increased.

A typical instance of the break-down or failure of a "law" or formula was brought out by Prof. Robt. A. Millikan (Nobel Laureate, Cal. Inst. of Tech.) in his work on weighing the electron. He caught electrons on colloidal oil droplets, and using the well-known formula of Sir C. G. Stokes calculated the increase in weight, after he had observed the added velocity of their fall. Now Stokes' formula is based on the assumption that the air or other fluid in which a sphere is falling, is *homogeneous*; and in most practical cases, air and water behave as if they were homogeneous. But the oil droplets used by Millikan were so tiny, that they fell through the "holes" between the air molecules. These holes are fixed by the molecular mean free paths, that is, by the average jumps of the molecules between collisions. Consequently, the droplets fell much more rapidly than Stokes' law said they should, and Millikan had to figure out and apply a correction.\*

### INTERFACIAL ANOMALIES†

In all free surfaces the exterior molecules occupy a position

\* See Millikan's book "The Electron"; also his paper in Alexander's "Colloid Chemistry," Vol. I.

† Among those whose work in this field is outstanding, may be mentioned Sir W. B. Hardy, G. Friedel, W. D. Harkins, I. Langmuir, N. K. Adam, Devaux. Papers by all but the last two are in Vol. I of Alexander's Colloid Chemistry, Theoretical and Applied. (Chem. Cat. Co. 1926.)

quite different from the interior molecules, which are on all sides surrounded by their own kind. Part of the attractive forces of the surface molecules are directed inward, part toward adjacent surface molecules (thus giving the effect of a surface skin), and a residual unsatisfied portion outward. This residual affinity may be demonstrated by cleaving a piece of mica (muscovite) and instantly putting the new surfaces together. They exhibit considerable cohesion, although this represents but a fraction of the original attractive force, and is soon lost by further adsorption of atmospheric constituents. A fresh iron surface absorbs atmospheric constituents so quickly that, although a piece of cast iron broken under mercury is amalgamated at its new surfaces, the same iron if broken above the mercury and instantly dropped in, is not amalgamated at all. (P. W. Bridgman.)

## CHAPTER III

### A SIMPLE PRINCIPLE UNDERLYING THE COLLOIDAL STATE—FORCES AFFECTING COLLOIDS

THE anomalous properties exhibited by matter in colloidal dispersion, as we follow it beyond the limit of microscopic resolvability to molecular dispersion, may be understood by considering two properties—(1) *specific surface* and (2) *kinetic activity*.

Specific surface (exterior or rind surface per gram) will vary considerably with the actual shape of the particles. If we assume an average spherical shape and plot specific surface against particle size, we obtain an hyperbola. For with infinitely large particles the free surface per gram approaches zero, and with infinitely small particles the free surface per gram approaches infinity; and the areas of spheres vary inversely as the squares of their radii. Therefore the curve is asymptotic to both axes and varies as  $d^2$ ; that is, it is hyperbolic.

The mean velocity of translation\* of particles is likewise subject to great variations; chemical nature, physical structure, viscosity of the dispersing medium, temperature; incidental ions, solutes, or impurities, all exercise their effects. But with the same substance, under the same conditions, the kinetic motion, beginning as the well-known Brownian motion at the limit of microscopic resolvability, increases at first slowly and then with gradually accelerating rapidity as subdivision proceeds; so that the curve of kinetic motion, plotted for convenience of comparison on the same axes as that of specific surface, soon rises rather abruptly, and cuts the latter (see Fig. 1). Motion tends to vary with *mass*, and the mass of a given substance varies inversely as the *cube* of the particle diameter (*i.e.*, as  $d^3$  or its *volume*).†

\* There is a kinetic motion of rotation as well as of translation, the observed translatory kinetic motion being a net result. The internal kinetics of particles is also a factor.

† The formulas for momentum ( $MV$ ) and for kinetic energy ( $\frac{1}{2} MV^2$ ), where  $M$  is mass and  $V$  is velocity, both depend on *volume*; for mass varies as volume varies, if density remains unchanged.

The kinetic motion curve, therefore tends toward a *cubic* hyperbola.

### THE ZONE OF MAXIMUM COLLOIDALITY

In following the gradual dispersion of a substance from gross visible particles all the way down to true molecular subdivision, it is obvious that in the colloidal zone there is a transition from a state where the kinetic activity is *small* as compared to the specific surface, to a state where the kinetic activity is *large* as

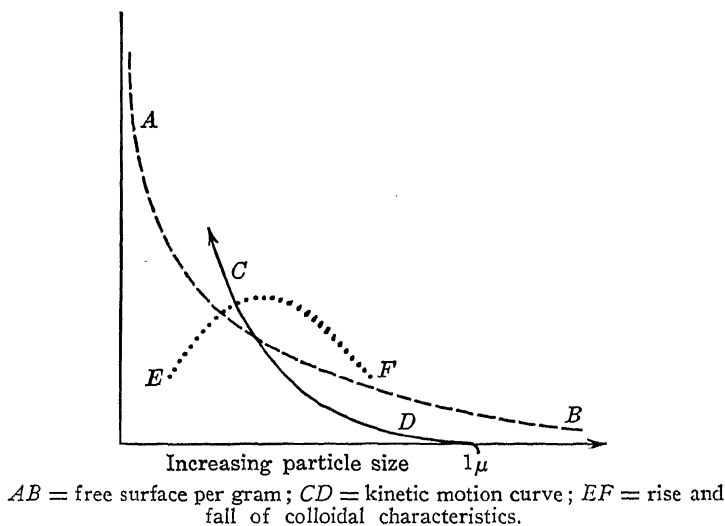


FIG. 1. Relation between kinetic activity and specific surface.

compared to the specific surface. In the heart of the colloidal zone there is usually observable an indefinite portion of the curve which has been termed the *zone of maximum colloidal* (J. Alexander, J. Am. Chem. Soc. 1920, 43, 434), wherein colloidal properties, such as viscosity, are most marked. (See p. 146.)

The zone of maximum colloidal appears in a wide variety of substances—in steel (J. Alexander), in duralumin (Merica, Waltenberg & Scott), in dyeing (R. Auerbach). In his H. M. Howe Lecture (before the Am. Inst. Min. & Met. Engr. 1924) Prof. Albert Sauveur stated facts which disclose its existence in heated steel, which showed maximum strength over a certain temperature range. On adding water to acetone solutions of nitro-

cellulose, F. Sproxton (3d Report on Colloids, etc., Brit. Assoc. Adv. Science, 1920) found that the viscosity rose to a maximum and then fell. Sulfur at  $150^{\circ}$  has a viscosity of 8; at about  $200^{\circ}$  it rises to over 50,000, and at  $400^{\circ}$  it drops to 150. Viscose in ageing passes through a maximum of viscosity.

Further instances are given in Alexander's Colloid Chemistry, Theoretical and Applied, Vol. I, from which the following quotation is taken (p. 25) :

"A most striking example of optimum dispersion is found in living matter. Figuratively speaking, if all chemical substances comprising our organism were in true or crystalloid dispersion, reactions would proceed so rapidly that we would, so to say, live ten years in ten minutes. On the other hand, if coarse dispersion prevailed, it would take ten years to live ten minutes. Every organism is dependent on the coordination of its reactions *in point of time*, and this leisurely procedure depends largely on *degree of dispersion*, which keeps chemical reaction velocities within certain speed limits through its regulation of free surface and kinetic activity. Life lies between lysis and coagulation. The colloidal zone is, as it were, a vital metronome tolling off the tempo of life."

Just before gases liquefy, they show, at the critical point, an opalescence, cloudiness, or turbidity, which Albert Einstein proved by sheer mathematical analysis, to be consequent on the existence there, under the action of the laws of probability (Boltzmann's Entropy Probability Theorem), of molecular aggregates of such size and number, that they scatter enough light to produce a Faraday-Tyndall effect, just as a searchlight does in a foggy atmosphere. The phenomenon is commonly seen when steam blows out into the air, as when a locomotive puffs. The bluish haze which appears just before the "steam" becomes white contains colloidal aggregates of the condensing water molecules. (See also p. 165 under Meteorology.)

We may therefore *pass upward* into the colloidal state as molecules *aggregate or become larger*, or *pass downward* into the colloidal state as coarse particles are *more finely ground or dispersed*. Thus Prof. Martin H. Fischer (University of Cincinnati) showed that in taking sodium salts of the fatty acids beginning with sodium formate and passing through the acetate,

propionate, etc., up to the stearate and oleate, we find that the water holding capacities of the salts increases steadily.\* His results may be tabulated as follows:

No of  
Carbon  
Atoms

1.....	Sodium formate.....	molecular dispersion
2.....	acetate	
3.....	propionate	
4.....	butyrate..	
5.....	valerate...	
6.....	caproate.....	shows signs of holding water
8.....	caprylate.....	1 mol. gives a jelly with 250 c.c. of water
10.....	caprate.	500 c.c.
12.....	laurate....	4,000 c.c.
14.....	myristate..	12,000 c.c.
16.....	palmitate..	20,000 c.c.
17.....	margarate.	24,000 c.c.
18.....	stearate...	27,000 c.c.
20.....	arachnate..	37,000 c.c.

On the other hand, Victor Lenher reduced silica to colloidal solution by continued grinding; and colloidal gold may be produced by the Bredig or the Svedberg method of electrical spattering, as well as by the Faraday-Zsigmondy method of reducing gold chloride. When an alcoholic solution of essential oils (*e.g.*, cologne, perfume) is poured into water, the oil is thrown out by the dilution of the alcoholic solvent and generally forms an opalescent colloidal emulsion. A similar effect appears on the dilution of alcohol which has been denatured with a water-insoluble solute—in fact, those who invite death by drinking such diluted poisoned alcohol call it “smoke”, because of the cloud that appears on dilution. Salts and acids favor the further aggregation and separation of the “oil”, which tends to float to the top, and this fact is taken advantage of in chemical analysis of perfumery, etc.

The above facts justify Svedberg's classification of methods for the formation of colloids into (a) *aggregation methods*, (b) *dispersion methods*.

There are, however, other possibilities for the formation of particles of colloidal dimensions. Some molecules are born col-

\*L. Lascary (Koll. Z., 34, 73 (1924)) found that the effect of sodium soaps on surface tension *increases* with molecular weight to sodium myristate, above which it *decreases*.

loids by virtue of their size; some achieve colloidity by aggregation or by chemical growth; and some have colloidity thrust upon them by dispersion or by the formation of an adsorption complex.

### CATALYSIS\*

Protagonists of the various views as to the nature of catalysis will, I think, all agree that close-range attractions between particles of any kind, be they electrons, protons, atoms, molecules, or small molecular groups, are consequent upon the outwardly directed unsatisfied residual fields of force, emanating ultimately from the electrically charged particles whose complexes (with uncharged units) constitute the chemical elements of which molecules and larger particles are made. Berzelius (*Jahresberichte*, 1836, 15, 237), to whom we owe the term catalysis, anticipated this aspect, for he said keenly:

It is then proved that several simple and compound bodies, soluble and insoluble, have the property of exercising on other bodies an action very different from chemical affinity. By means of this action they produce, in these bodies, decompositions of these elements and different recombinations of these same elements to which they themselves remain indifferent.

This new force, which was hitherto unknown, is common to organic and inorganic nature. I do not believe that it is a force quite independent of the electrochemical affinities of matter; I believe, on the contrary, that it is only a new manifestation of them; but, since we cannot see their connection, and mutual dependence, it will be more convenient to designate the force by a separate name. I will therefore call this force the catalytic force, and I will call catalysis the decomposition of bodies by this force, in the same way that one calls by the name analysis the decomposition of bodies by chemical affinity.

The ordinary "zipper" or "talon" closure, now in common use on bags, tobacco pouches, arctics, sweaters, and similar articles of clothing, has a "key", which, when drawn in one direction, massages the opposing "hooks" into a position where they engage each other and hold firmly. Reversing the motion of the key, the opposing hooks are disengaged, and as the key slides along, the closure is opened. The action of the key is analogous to that of a catalyst, and in fact, as was shown by A. Croft Hill

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\* See J. Alexander, *J. Chem. Education*, 1932, 9, 2026. See also the index, under "Enzymes."



as far back as 1898 (J. Chem. Soc., 1898, 73, 634), the action of catalysts may be a reversible one. He worked with an enzyme, yeast maltase, and built up from dextrose a disaccharide, at first thought to be maltose, but later shown to be isomaltose.

The analogy with the "key" may be carried further. There is a mechanical specificity between the key and the hooks which it can influence. At temperatures approaching the softening point of the metal comprising the key or hooks, we would expect the opening and closing processes to fail. Prolonged use of the key might wear it to such an extent that it could no longer function, so that there would be some limit to the number of hooks which any key could open and close. Again, an adhering bit of solder, or paint, or chewing gum might prevent the key from moving, or some deformation of the hooks might hold it fast. In like manner, catalysts are specific in their action, and have a "life". They may be worn out, "fused", temporarily or permanently masked or poisoned.

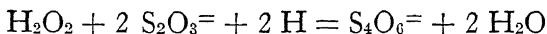
Most books on catalysis distinguish between *homogeneous catalysis*, occurring in homogeneous dispersions, and *heterogeneous catalysis*, which occurs at demonstrable interfaces. A moment's consideration will show, however, that since gases and liquids consist of discrete particles (atoms, molecules, or groups of these), *all* catalysis is essentially heterogeneous. In gases and liquids we simply reach a limiting case in the degree of dispersion of the catalyst and/or reactants, so that the temporary or transient intermediate groupings of catalyst and reactants are, in these cases, generally stoichiometric, and may be regarded as unstable chemical compounds.\* As catalysts become complex and appear in larger and still larger masses, the sharp definiteness of chemical combination between catalyst and reactants begins to give way to the dominance of specific electronic surface contours of the catalyst, which represent a mosaic of the outwardly directed unsatisfied electronic fields of the atoms and molecules in the active interface. The sharp definiteness of stoichiometric relations tends to be replaced by a statistical or mosaic average relationship, which may at times simulate some stoichiometric compound. The X-ray spectrometer should be helpful in differentiating between the two classes of compounds, though this will be largely

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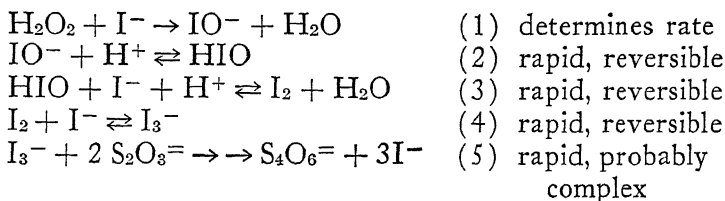
\* The author expressed this idea in an unpublished Master's Thesis (1899).

a matter of our own definitions, rather than of any basic natural difference.

A typical case of homogeneous catalysis is the oxidation of thiosulphate ion by hydrogen peroxide in slightly acid solution by the iodine-iodide couple. As pointed out by Kolthoff and Livingston (*Ind. Eng. Chem., Anal. Ed.*, 1935, 7, 209) the stoichiometric reaction represented by the equation



is the summation of five reaction steps, the rate of the whole reaction being determined by the velocity of the first of these:



Here the iodine is alternately oxidized and reduced. The rate of oxidation of thiosulphate ion by iodine is extremely rapid, and hydrogen peroxide oxidizes iodide ion more rapidly than it oxidizes thiosulphate ion.

Because of the complicated and thermolabile structures both of catalysts and of the substances on which they act, this "key" concept is merely indicative of the gross joining or severance of any two particulate units by a catalyst. In any actual practical case we are confronted with the effects of many other factors, *e.g.*, variations in the surface contour of the catalyst and of the reactants, yielding areas of optimum and of null activity, the presence of myriads of potentially reactive particles, of diluent molecules of the dispersion medium (solvent, air), and of effective "impurities" (promoters, poisons).

From what the spectroscope reveals regarding the numerous, extensive, and specific activities in the internal kinetics of atoms at high temperatures, we are justified in believing that even at lower temperatures a considerable portion of the energy of thermal agitation is absorbed within atoms and molecules, producing specific changes in the energy positions of their constituent

particles. No doubt the energy thus absorbed bears a most intimate relation to the specific heat of any substance.

Temperature is, then, an important factor in catalysis; but what we measure and call the temperature of any system represents an integration of the kinetic activities of all its constituent particles over a period of time sufficient to affect some recording instrument (thermometer, thermopile). During this interval, and indeed at any instant, the internal electronics and the particulate rotation and free path motion of individual particles will be widely different. The activities of any one particle will vary widely from one instant to another. The question naturally arises as to whether we can speak of any *individual* particle as having any *measurable* temperature, or, in fact, any *lasting* temperature at all. At any instant, only a portion of the particles would exist in a state of "excitation" or "activation" (see p. 10) permissive of certain specific changes. It is interesting to note that various types of radiation (light, X-rays, ultraviolet rays) may produce marked internal particulate activation without determinable increase in temperature.

Perforce, we rely on statistical averages in our measurements of the net results of catalysis as well as of temperature, but a correct understanding of the mechanism whereby these results are attained is essential to the control of the operative factors. The average wealth *per capita* is no measure of the efficiency of a government or of the happiness of its people, for some different distribution might lead to greatly increased total wealth and individual happiness.

### CRITICAL VELOCITY

At the Toronto meeting of the British Association for the Advancement of Science (1925), Sir Ernest Rutherford, in order to illustrate the repulsion of a positively charged alpha particle by a positively charged nucleus, made use of an electro-magnet swung from the ceiling with its positive pole down, and another similar magnet fastened to a table beneath, with its positive pole up. If the swinging magnet passed sufficiently near the fixed one, it was swerved from its course. In attempting to show that a direct, head-on hit would result in a repulsion, the magnet was swung from too far back on the first attempt, with the result that

its high velocity carried it over the fixed magnet. A second, less violent swing, resulted in a rebound.

This observation gave rise to the following reasoning: Suppose we turn upward the *negative* pole of the magnet on the table, and try swinging the positive pole of the other magnet over it at varying velocities. It is obvious that while at low speeds, the swinging magnet will be *held* by the fixed one, there is some critical speed above which it will swing past and *not* be held.

This same factor of *critical velocity* makes itself felt in many catalytic and enzyme actions, which, in general, proceed more rapidly with rise of temperature, up to a certain point varying with the particular case; after which further increase of temperature results in a decline in activity. We may here consider that throughout, increase in temperature brings about an increase in the *total number* of the essential molecular impacts or meetings; but that after reaching the critical temperature, owing to increase in average molecular velocities, the number of *successful* molecular meetings begins to diminish. To put it figuratively, a catalyst resembles a Judge who may marry or divorce molecules, if they appear before him and do not rush off without waiting for "due process of law." And like the Judge, a catalyst may become "tired," or buried under other matters, and refuse to consider the domestic relations of waiting molecules.

*Supersonic vibrations*, produced by electric oscillations in quartz crystals with apparatus designed by Prof. Langevin (Paris), can produce *emulsions* and facilitate reactions of various kinds. The total amount of energy in sounds is relatively small, as may be seen from the estimate of the late Prof. Arthur Gordon Webster (Clark University) that it would take approximately ten million cornets playing *fortissimo* to emit one horse-power of sound. Recently E. W. Flosdorf, L. A. Chambers, and W. M. Malisoff, (J. Am. Chem. Soc., 1936, 58, 1069), reported that audible or *sonic* vibrations influence some chemical reactions.

## THE RELATION OF COLLOIDAL TO OTHER FORCES

Mendeléef in his suggestive paper, entitled "A Chemical Conception of the Ether," intimated that gravitation might be explained on the basis of ethereal impact acting from all sides;

for from this assumption the Newtonian laws of gravitation may be easily developed. This is evident from the following considerations:

Assuming that the ether is a subtle gas whose particles move with approximately the speed of light, and that mass represents the ability of a substance to reflect the motion of ether particles, then any body, if alone in the universe, would be struck equally on all sides by the ether particles and if at rest would remain at rest, but if in motion would tend to maintain its rate of motion. This is *Newton's first law*; but it is obvious that if the motion of the body is large as compared with the motion of ether particles, then the moving body will appreciably increase in mass; for it will anticipate the blows of ether particles coming from the direction of its motion, and receive a diminished impact from those coming from the opposite direction (*relativity effect*).

As soon as we introduce a second body into our calculation, then each body *shadows* the other *in proportion to its mass* or ether-stopping capacity. This means an excess of ether pressure on the unshadowed side, so that the bodies attract each other directly as their masses. But since the areas of spheres vary inversely as the squares of their radii, it is obvious that a body removed to twice the distance will have only  $1/4$  the shadowing effect; at three times the distance only  $1/9$  the shadowing effect, etc. That is, the attraction between the bodies *varies directly as their respective masses and inversely as the square of the distance between them* (*Newton's second law*).

E. Cunningham ("Relativity and the Electron Theory") has shown that a material ether is not inconsistent with relativity, and the objective view of gravitation is much more appealing than recourse to "fields of force" without a material substratum, although, as Herbert Spencer pointed out, explanations of this kind simply transfer the enigma of Nature one step further back.

M. Le Sage in 1784 had expounded the same theory of gravitation, and Prof. S. P. Langley had a translation of Le Sage's work published by the Smithsonian Institution. It is possible that the nature of chemical attraction may be explained as a gravitational force modified because the reacting units are so close together that their size, shape and internal structure become

material factors. We seem to be working toward the view maintained by Faraday and no doubt by many others, that there is one ultimate kind of force or energy. The modern physicist regards matter and energy as being interconvertible, but the evidence may be also interpreted as representing the building up or the breaking down of material groups, the ultimates always eluding us. In January 1929 Albert Einstein published his "unified field theory" wherein he combines the gravitational field formulae of his general theory of relativity, with J. Clerk Maxwell's vector formulae covering the electro-magnetic fields of light.

P. V. Wells (J. Wash. Acad. Sci. 1919, 9, 361) suggests the following classification of forces:

1. *Electronic Forces*—Maintain positive nucleus, and negative or valence electrons in equilibrium as a single system.

2. *Atomic Forces*—Maintain two or more atoms in equilibrium as a single system.

3. *Molecular Forces*—Maintain two or more molecules in equilibrium as a single system.

4. *Molar Forces*—Maintain two or more masses in equilibrium as a single system.

*Nuclear forces*, active within the close confines of atomic nuclei, are now being evaluated; they bind electrons, protons, neutrons, etc., into atomic nuclei.

Electronic forces are thus responsible for atoms; atomic forces, for their chemical combination into molecules; molecular forces, for most physico-chemical and colloidal phenomena; and molar forces, for ordinary physical and astronomical phenomena. "Each group of forces," says Wells, "may be regarded as the residual fields of force remaining unsaturated in the smaller systems constituting the components of the system under consideration. . . . Molecular systems have lost so much of their discreteness that combinations of molecules do not follow the laws of definite and multiple proportions. In such phenomena as molecular association and surface structure, the discreteness of atomic constitution begins to give place to statistical continuity. Moreover, in these phenomena the forces are relatively so weak that molecules are not usually regarded as permanently grouped together."

Thus adsorption and molecular association would be considered as molecular phenomena; and while polymerization and condensation may start that way, in them atomic forces predominate.

In reading over the numerous practical applications of colloid chemistry we will later consider, it must be remembered, then, that most of the reactions lack that preciseness indicated by the present meaning of the term "chemical compound." Slight deviations from previous conditions may involve a material difference in results, and until we understand and can give proper weight to all the underlying factors, many of our successful methods will remain "cooking recipes." Colloid chemical research is letting in a flood of light upon many reactions not amenable to the ordinary stoichiometric laws of chemistry, though in some cases they may closely approach these laws.

#### THE IMPORTANCE OF "IMPURITIES" \*

The average student is apt to consider himself outrageously treated if he is held to account for not discovering and estimating say  $\frac{1}{2}\%$  of some element in an "unknown". However, if he only looks into the chemical demands of business and industry, he will appreciate the wisdom of his teachers; for the success or failure of a process or a product, and even freedom from jail may depend upon analytical determinations running into ten thousandths of one per cent. For example, the present tolerance for arsenic in food products allowed by the U. S. authorities is 0.018 grain per pound, which is 258 millionths of one per cent. Selling a food with a higher percentage exposes the seller to criminal charges.

But small traces of "impurities" are often beneficial, and without them a product may become less desirable or even worthless. Thus when Auer von Welsbach patented the incandescent gas mantle, he claimed what was *then* believed to be pure thoria. Subsequent improvements in analytical methods proved, however, that chemically pure thoria gave no light, but that the efficiency of the Welsbach mantle was due to 1 per cent. of ceria present as an impurity in the thoria of those days in just the amount to

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\* See J. Alexander, J. Soc. Chem. Ind. 1917, 36, 7-9; Ind. Eng. Chem., 1923, 15, 190.

give the brightest light. With 5 per cent. ceria the light is very weak. Incidentally, the Court upheld the Welsbach patents, because in them he referred to the product *then known* as thoria. Patents must be read in the light of the technical knowledge existing at the time they are taken out. Nitrocellulose products insoluble in our modern highly purified methanol were nevertheless soluble in the "wood spirits" referred to in early patents, for the crude product then contained as impurity ketones which made it a solvent for nitrocellulose.

In many cases "impurities" assume the colloidal state and act as catalysts, as coloring agents, as colloidal protectors, as inhibitors of catalysis or of crystallization, etc. Generally, *the behavior of mixtures* is quite different from the average of the properties of the substances mixed—witness the case of solder, which melts far below the melting points of its constituents, lead and tin. By way of illustration a few cases where impurities are important, will be epitomized under two headings.

#### TROUBLESOME TRACES

*Soap*—1 part of sulphur per million in coconut oil gives soap prone to rancidity.

*Tanning*—traces of copper or iron throw white leathers "off shade."

*Dyeing*—traces of iron in alum dull the shade of Turkey red, and of most color lakes.

*Paper*—iron in the digester discolours the batch.

*Lead-burning*—traces of arsenic in the hydrogen used, prevent the formation of good welds.

*White Lead*—traces of silver produce a pink tone; of copper, a greenish tone.

*Foods*—less than one part of copper per million in coffee can be tasted, and one part of copper in 40 million in butter gives measurable increase in oxidative rancidity.

*Brewing*—traces of iron make "ink" with the tannin of the hops, and the bluish iron tannate turns "Pilsner" beer a sickly green.

*Hydrogenation*—traces of bromine absorbed by phenol from the air of the laboratory prevent its hydrogenation; thiophene in benzene prevents its hydrogenation to cyclohexane (Sabatier).



*Dry Batteries*—iron in pyrolusite ( $\text{MnO}_2$ ) and copper in sal ammoniac ( $\text{NH}_4\text{Cl}$ ) are both harmful to battery "life."

*Metals*—*Gold*—is rendered brittle by 0.05 % of lead. 0.216% arsenic reduces the conductivity of copper 39%. *Most metals are sold on the basis of carefully regulated allowances* of "impurities." Twenty years ago the purest iron had a magnetic permeability of only 16,000, as against 280,000 shown by highly purified iron to-day.

The potency of catalyst "poisons" was referred to by H. A. Bernthsen (Eighth Int. Cong. Applied Chemistry 1912) in his address on the Haber process for synthesis of ammonia. Sulphur, selenium, tellurium, phosphorus, arsenic, boron or the compounds of these elements such as the hydrides, and also many carbon compounds and certain metals of low melting point such as lead, bismuth and tin, may all act as poisons to the iron catalyst. Sulphur dioxide is very poisonous. Bernthsen stated: "Extremely minute quantities of these bodies, which are almost always present even in the purest commercial products or in so-called pure gases, suffice to render the catalysts absolutely inactive or at least to diminish their activity very seriously. Thus iron, for example, prepared from ordinary iron oxide with a content of one per thousand of sodium sulphate is, as a rule, inactive. Iron containing 0.1 % sulphur is generally quite useless, and even with 0.01 % is of very little use, although in appearance and when examined with the ordinary physical and chemical methods no difference at all can be detected as compared with pure iron."

"The recognition of these facts gave rise to two problems: (A) The preparation of contact masses free from poison or the removal of such poisons from them; and (B) freeing the gases to be acted upon catalytically from all contact poisons. A trace of sulphur, one part per million, in the gas mixture, can under certain conditions be injurious, so that even electrolytically prepared hydrogen must generally be further specially purified."

Many substances are so toxic or otherwise objectionable that traces must be avoided. Lead is a *cumulative* poison, and the poisonous effects of long exposure to small amounts of benzene have recently been recognized. In making sulphonal there is

produced a mercaptan whose odor is described as appalling, and so powerful that one four-hundred millionth of a milligram may be detected. A small bottle of mercaptan, broken in a certain laboratory, rendered the building uninhabitable for days.

### HELPFUL TRACES

*Iodoform*—is ineffective in the absence of impurities which catalyze its decomposition to give free, active iodine.

*Rubber*—crude Para contains nitrogenous substances which facilitate the "cure"; the purer plantation rubber demands "accelerators."

*Brass*—a small amount of lead prevents "chattering" in the lathe. (Antimony and bismuth even in small traces are very bad.)

*Copper*—traces of arsenic aid in the rolling of tubes and sheets. Tubes *free* from arsenic corrode ten times as fast as those with arsenic.

*Radio Tubes*—traces of certain oxides increase the life of the filament.

*Electroplating*—small amounts of "addition agents" in the bath produce smooth deposits.

*Gasoline*—0.06% of lead tetra-ethyl inhibits "knock."

*Brewing and Baking*—traces of lime salts aid the growth of yeast. "Arkady flour" for bakers, named after Prof. Robert Kennedy Duncan (RKD), contained much gypsum; and the patents for "Burtonizing" brewing water called for addition of lime salts. Traces of proteolytic enzymes prevent cold-cloud in beer (see p. 233). The use of sodium bromate as a "yeast food" is said to have saved a large baking company over \$500,000 a year by cutting its purchases of yeast in half.

*Biology*—Traces of copper (5 to 60 parts per 100,000,000 of sea-water) are essential before the free-swimming oyster larvae will "set" and become transformed into "spats."

*Agriculture*—traces of many elements are essential to the growth and well-being of plants—*e.g.*, manganese, boron, zinc, etc.

The properties of steel are greatly affected by small amounts of many elements or compounds. Phosphorus is harmful, but 0.15% of vanadium gives an unbelievable increase in strength and toughness. Traces of copper (*e.g.*, from "grandma's copper preserving kettle") inhibit bacteria and moulds, and minute amounts of copper sulphate have been used to kill troublesome algae, etc. in reservoirs. While our foods must be *nearly* free from certain poisons, such as arsenic, copper, fluorine, iodine, zinc, etc., we actually need iodine for our thyroids and fluorides for our teeth. The average hen's egg contains a milligram of zinc. V. Birckner (J. Biol. Chem. 1919, 38, 191), found in human milk 12 parts of zinc per million, and in cows' milk about 4.5 parts). The U. S. Bureau of Fisheries asked that seafoods be exempted from certain general restrictions under the Food and Drugs Act because some of them (shrimp, oysters) often contain arsenic and copper in excess of the tolerances allowed, and furthermore because the arsenic is apparently combined organically and is not as toxic as the inorganic arsenic derived *e.g.*, from insecticides used in spraying fruit trees.

In 2½ years operation the Ethyl-Dow Co. (near Wilmington, N. C.) extracted 10,000 tons of bromine by processing over 154 million tons of seawater. Incidentally, 0.098 tons of gold passed through the plant to the ocean again, indicative of the difficulty of the profitable extraction of gold from the ocean. On the other hand, an ascidian, *Phallusia*, accumulates vanadium from the ocean in its blood pigment, and workable deposits of vanadium seem to have originated from biological concentration of small traces.

There is a real danger, if pure food regulations are carried to an unreasonable degree, that our daily diet may be deficient in the trivial amounts of "poisons" essential to our well-being. Polished rice brings beri-beri as a vitamin-deficiency disease. On chemically pure food we would "dwindle, peak, and pine"—impurities are our salvation. Still, we must avoid taking too much of any of them at once; a sufficiently large dose of ordinary salt can produce serious consequences. The "peck of dirt" that each person is said to eat during his life must be taken in unnoticeable and innocuous installments, and we must be especially careful with cumulative poisons, like lead. In considering poisons, the

*quantity* of the food eaten is a material factor, commonly not considered. Thus the 5 parts of lead per million sometimes found in lobster, would be very serious if in bread or milk. While we do, somehow or other, manage to get fluorine for our teeth, an outbreak of "mottled teeth" was traced to the presence of too large a "trace" of fluorine in drinking water; one or two parts per million almost blacken the upper front teeth.

### SOLUTION VS. COLLOIDAL SOLUTION

When the attraction of the molecules or ions of a liquid for those of a solid exceeds the attraction of the molecules or ions of the solid for each other, then the solid is dissolved or peptized by the liquid. If the dispersion is profound enough, the solute may go into true or crystalloidal solution, but if the molecules of the solute cling to each other to a considerable extent, they may form groups of colloidal dimensions, and there results a colloidal solution.\*

The degree of dispersion in which a substance exists in a solution naturally affects its kinetic activity, its speed of diffusion, and even its ability to diffuse. Thus sodium stearate is not a good protector (see p. 153) nor even a good detergent until it is dissolved in sufficiently heated water; and in tanning and dyeing the degree of dispersion of the tanning or dyeing agent governs the amount and speed of its fixation. In the case of a kinetically balanced equilibrium, as with blood sugar, difference in diffusion speed may raise or lower the percentage of dextrose existing in the blood at any instant.

An interesting case is the action of selenium oxychloride on barium sulphate. As Prof. Victor Lenher discovered (J. Am. Chem. Soc., 1921, 43, 29-35), this remarkable solvent, which dissolves such diverse substances as rubber and gelatin, converts the highly insoluble barium sulphate into a colloidal jelly. Molecular groups having a great tendency to dissolve are sometimes able to drag into solution with them attached groups which would otherwise be insoluble, and are sometimes called "sol formers." Thus many aniline dyes and even oils are sulphonated in order to

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\* Indeed, with most solutes and with most solvents, too, there is a certain degree of molecular association, as it is called. Liquid water is mainly dihydrol ( $\text{H}_2\text{O}$ )<sub>2</sub>. Some molecules are themselves of colloidal size.

make them "soluble" in water, where they usually form colloidal dispersions.

### SURFACE FORCES IN GRINDING OR PULVERIZING

It is not an easy or inexpensive operation to dry grind most substances below 200 mesh. As subdivision proceeds, the total free surface increases enormously, and apart from the inherent difficulty of breaking up a very fine particle, the tendency of the fragments to reunite or "cake up" begins to assert itself. The finer the particles the greater this tendency, and it is increased by pressure. It is to a large measure overcome by wet grinding, because the adsorption of fluid or solutes at the new surfaces tends to prevent their reunion.

### THE "COLLOID" MILL

This is essentially a high speed disintegrator with close clearances, arranged for wet grinding, and the patents relate chiefly to mechanical details. A readily absorbable substance (a defloculator or protective colloid) is added to the liquid in the mill, and stabilizes the colloidal dispersion as it is formed.

One machine has a very high speed rotor eccentrically placed in a casing of circular cross section. The high peripheral speed of the rotor forces the material to be pulverized, practically under pressure, into the space between the rotor and the casing, where most of the atomization occurs, the material to a large extent grinding against itself.

Colloid mills can be used to make some emulsions, *e.g.*, oil, asphalt and colloidal solutions of cellulose and highly concentrated colloidal mercury have been made with them. It is said to be used in the soap industry for speeding up saponification; in the dairy industry for homogenizing milk and cream; in producing colors, inks, rubber goods, etc. No doubt it will produce many desirable results, but since high speed takes power and means wear, the commercial advantages of the mill remain to be demonstrated. (See *e.g.*, 8th Report on Progress of Applied Chemistry, Soc. Chem. Ind., 1923, page 340.)

Some years ago a so-called "colloid mill" was demonstrated before a technical-scientific gathering; dried milk powder mixed

with water was reconverted into milk, a cresol-soap solution was made into an emulsion with water, and a red pigment converted into a suspension which promptly settled out. After the burst of applause which followed this evidence of the potency of the mill, discussion was called for; and some one had the temerity to point out (1) that simple stirring with a teaspoon would suffice to reconvert the milk powder into milk; (2) that simple stirring in a bucket of water with a stick would suffice to make an equally perfect emulsion of the cresol-soap solution; (3) that the red pigment suspension had already settled out, and was therefore not colloidal. This awoke the audience to the fact that, in many cases at least, satisfactory results may be had by intelligent use of simple, well-known apparatus, without any need of paying extravagant prices or royalties. Indeed, the proper preparation of what goes into the apparatus is generally of much greater importance than the type of mill used.

The literature describes a large number of colloid mills and other dispersing or emulsifying apparatus (see *e.g.*, Dr. Wm. Clayton's book on "Emulsions and Emulsification," and his paper in *Chemistry and Industry*, 1932, 51, 129-39; also Dr. A. Chwala's paper "Colloid Mills and Comminution Chemistry" in Vol. III of Alexander's *Colloid Chemistry*). Chwala distinguishes five steps in the dispersion of a solid or gel in a fluid medium: (1) suspension; (2) cloudy dispersion; (3) colloidal dispersion; (4) complex formation between solid and fluid; (5) true solution. Cloudy dispersions are important *e.g.*, in ore-flotation, paints and lacquers, papers (including carbon papers). Chwala also points out the importance of peptizers or dispersing agents, and finds that sodium pyrophosphate is a good disperser for solid non-gels.

## CHAPTER IV

### CLASSIFICATION OF COLLOIDS

THE broadest classification of colloids is that of Wolfgang Ostwald (*Koll. Zeitschr.*, 1907, 1, 291), who grouped them according to the physical state (gaseous, liquid or solid) of the subdivided substance (dispersed phase), and of the medium in which the particles of the subdivided substance are distributed (dispersion medium).<sup>\*</sup> Table IV below shows the nine resulting groups and gives some instances of each.

TABLE IV

Dispersed phase	Dispersion medium	Example
Gas.....	Gas.....	No example, since gases are miscible in all proportions.
Gas.....	Liquid.....	Fine foam, gas in beer.
Gas.....	Solid.....	Gaseous, inclusions in minerals (meerschäum, pumice), hydrogen in iron, oxygen in silver.
Liquid.....	Gas.....	Atmospheric fog, clouds, gases at critical state.†
Liquid.....	Liquid.....	Emulsions of oil in water, cream, colloidal water in chloroform.
Liquid.....	Solid.....	Mercury in ointments, water in paraffin wax, liquid inclusions in minerals.
Solid.....	Gas.....	Cosmic dust, smoke, condensing vapors (ammonium chlorid).
Solid.....	Liquid.....	Colloidal gold, colloidal sodium chlorid, colloidal ice in chloroform.
Solid.....	Solid.....	Solid solutions, colloidal gold in ruby glass, coloring matter in gems.

Ostwald's classification, however, is more theoretical than practical, for the properties of colloids are dependent mainly upon the specific nature of the dispersed substance and its degree of subdivision. Following Hardy, Zsigmondy divided colloids

<sup>\*</sup>G. Bredig proposed to call colloids "microheterogeneous systems." Wo. Ostwald called them "dispersed heterogeneous systems," which expression was contracted by P. P. von Weimarn into the term "dispersoids."

†A. Einstein, "Turbidity near the Critical State," *Ann. Phys.*, 1910, 33, 1275; also Alexander, Vol. I, p. 323.

into two classes, the *reversible* and *irreversible*; the former redissolve after desiccation at ordinary temperatures, whereas the latter do not. Often, the addition of reversible colloids will make an irreversible colloid redissolve after desiccation. (See p. 151.)

Table V, taken from Zsigmondy,\* illustrates this classification, and shows how colloids having the same particle size or degree of subdivision may nevertheless act quite differently because of specific differences in the nature of the dispersed substances.

With the reversible colloids (gelatin, gum arabic, albumen), there is a more intimate union between the two phases; in fact it is probable that with them we have really a mixture of (1) a dispersed phase of water subdivided in the solid, with (2) a dispersing phase of the solid finely subdivided in water. The reversible colloids are therefore called *emulsoids* and the irreversible colloids *suspensoids*. Colloids of the reversible type are also said to be *hydrophile* or *lyophile*, while the irreversible colloids are *hydrophobe* or *lyophobe*.†

No sharp line is to be drawn, however, for besides intermediate or transition cases between the two classes, there may be recognized two groups of irreversible colloids, roughly defined by their behavior upon concentration:

*First:* The *completely irreversible*, which coagulate while still quite dilute and separate sharply from the solvent with the formation of a pulverulent precipitate rather than a gel (*i.e.*, pure colloidal metals). Chemical or electrical energy is needed to bring them back again into colloidal solution.

*Second:* The *incompletely reversible* which, when quite concentrated, form a gel that may be easily redissolved or *peptized* by comparatively small amounts of reagents, unless the evaporation has proceeded too far (*i.e.*, colloidal stannic acid).

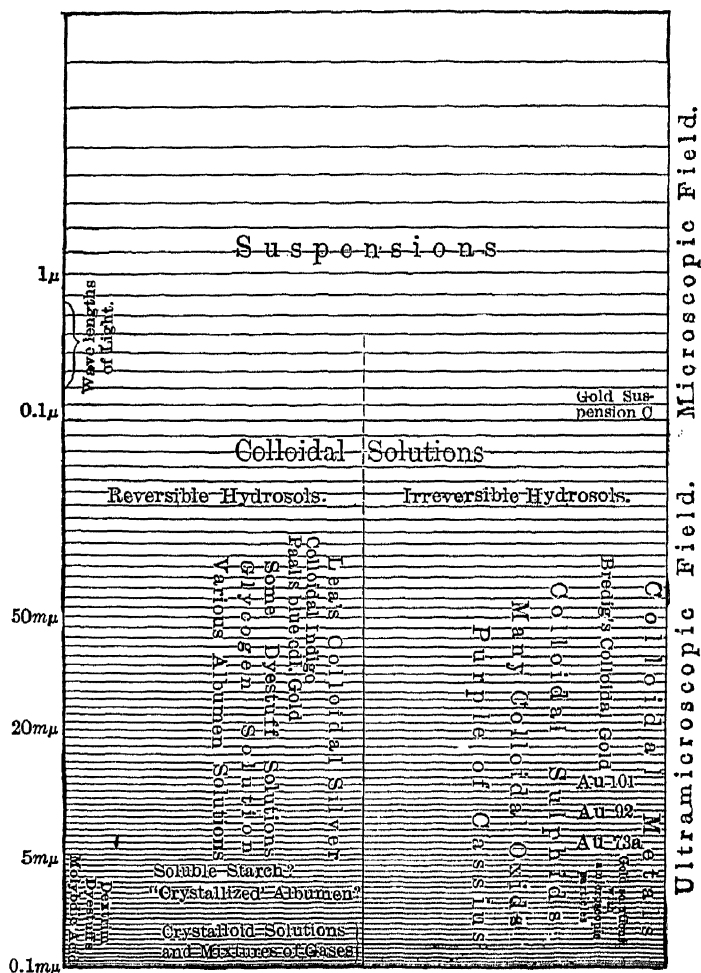
It is possible for the molecules of a substance to undergo aggregation or polymerization *in part*, yielding colloidal groups of the substance or polymer dispersed in the unchanged sub-

\* "Colloids and the Ultramicroscope," J. Wiley & Son, Inc. (Translation by J. Alexander.)

† Hydrophile = water-loving; hydrophobe = water-hating. Lyophile = solution-loving; lyophobe = solution-hating.



TABLE V



### *Classification of Colloidal Solutions*

according to the size of the particles contained in them and  
according to their behavior upon desiccation.

stance. Such a dispersion is termed an *iso-colloid*. A practical example is a dispersion of colloidal ice crystals in ice-cold water, the much-dreaded "frazil" as it is called in Canada where it sometimes causes much trouble in hydroelectric plants by accumulating like a slimy precipitate in the intake and then "coagulating" and obstructing the flow of water. See Prof. H. T. Barnes (McGill University), in Alexander's Colloid Chemistry, Vol. I, p. 437

## CHAPTER V

### CONSEQUENCES OF SUBDIVISION

As THE subdivision of a substance proceeds, the area of its effective surface increases enormously, as may be seen from the following Table VI adapted from Ostwald. Consequently surface forces, such as adsorption, capillarity and surface tension, become enormously magnified and of primary importance. Furthermore, the so-called radius of molecular attraction ( $\rho = 50m\mu$ ) is well within the colloidal field, so that the specific attractive forces of the particles also enter as a controlling factor. In fact, before substances can unite chemically their particles must be first brought into proper subdivision and proximity,\* by activation; solution, fusion, ionization or even by mere pressure, as was demonstrated by W. Spring,† who caused fine dry powders to combine chemically by high pressure.

A trace of water is often necessary to initiate reactions. Dry sodium is not attacked by dry chlorine, and anhydrous hydrofluoric acid is now shipped in steel tank-cars. Ordinary "dry" corn starch (about 12% moisture) must be super-dried when used as a diluent in baking powders, to prevent the acid ingredient (alum, acid phosphate, cream of tartar) from reacting with the sodium bicarbonate which yields the leavening gas.

If the degree of subdivision is not profound enough to permit of the combination of isolated atoms or ions with each other, chemical combination in the strict sense may not occur, but there may be produced "adsorption compounds" resulting from the union of atomic or ionic mobs in indefinite or nonstoichiometric proportions, under the influence of more or less modified chemical forces. The combination of arsenious acid and ferric oxid which Bunsen regarded as a basic ferric arsenite,  $4\text{Fe}_2\text{O}_3, \text{As}_2\text{O}_3, 5\text{H}_2\text{O}$ ,

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\* M. Raffo and A. Pieroni observed that colloidal sulphur reduced silver salts energetically, whereas even fine precipitated sulphur did not form silver sulphide in the cold, and did so only partially upon boiling.

† In 1914 the Société Chimique de Belgique gathered and reprinted the work of this brilliant and prolific investigator, in two large volumes.

has been shown by Biltz and Behre to be an adsorption compound; and Zsigmondy proved "purple of Cassius" to be an adsorption compound of colloidal gold and colloidal stannic acid by actually synthesizing it by mixing the two separate colloidal solutions. The colloidal tin acts as a protector for the colloidal gold. Zsigmondy's proof has been further confirmed by A. Huber (*Physikal. Zeit.* 1924, 25, 45) who examined the purple of Cassius with the X-ray spectrometer and found that none of the gold is in chemical combination.

The effect of increasing subdivision upon the particles in colloidal solutions is illustrated in Table VII, adapted from Zsigmondy. Tables IX and X were prepared by Zsigmondy to illustrate visually the relation of the sizes of colloidal particles to well-known microscopic objects on the one hand and to the theoretical sizes of molecules on the other.

TABLE VI. RESULT OF PROGRESSIVE DECIMAL SUBDIVISION OF A CUBE

Means of Perception	Length of edge.	Typical object.	Number of cubes.	Total surface.
Eye—(Visible)	$\left\{ \begin{array}{l} 1 \text{ cm.} \\ 1 \text{ mm.} \end{array} \right\}$	Small Peas	1	6 sq. cm. = 0.93 sq. in.
		Fine Shot	$10^3$	60 sq. cm. = 9.3 sq. in.
Microscope	$\left\{ \begin{array}{l} 0.1 \text{ mm.} \\ 0.01 \text{ mm.} \end{array} \right\}$	Talcum Powder	$10^6$	600 sq. cm. = 93 sq. in.
		Amoeba	$10^9$	6000 sq. cm. = 6.46 sq. ft.
	$\left\{ \begin{array}{l} 1 \mu \\ 0.1 \mu \end{array} \right\}$	Small Bacteria	$10^{12}$	6 sq. m. = 64.58 sq. ft.
		Large Colloid Particle	$10^{15}$	60 sq. m. = 645.83 sq. ft.
Ultramicroscope	$\left\{ \begin{array}{l} 0.01 \mu \\ 0.01 \mu \end{array} \right\}$	Large Molecule	$10^{18}$	600 sq. m. = 6458.33 sq. ft.
X-ray Spectrometer	$\left\{ \begin{array}{l} 1 m\mu \\ 0.1 m\mu \end{array} \right\}$	Molecules	$10^{21}$	6000 sq. m. = 1.48 acres
		H Molecules	$10^{24}$	6 hectares = 14.83 acres
	$0.01 m\mu$		$10^{27}$	60 hectares = 148.26 acres
	$*0.001 m\mu$		$10^{30}$	6 sq. kilometers = 1482.6 acres = $2\frac{1}{3}$ sq. miles

\* These subatomic dimensions are 1000 times larger than the theoretical size of electrons

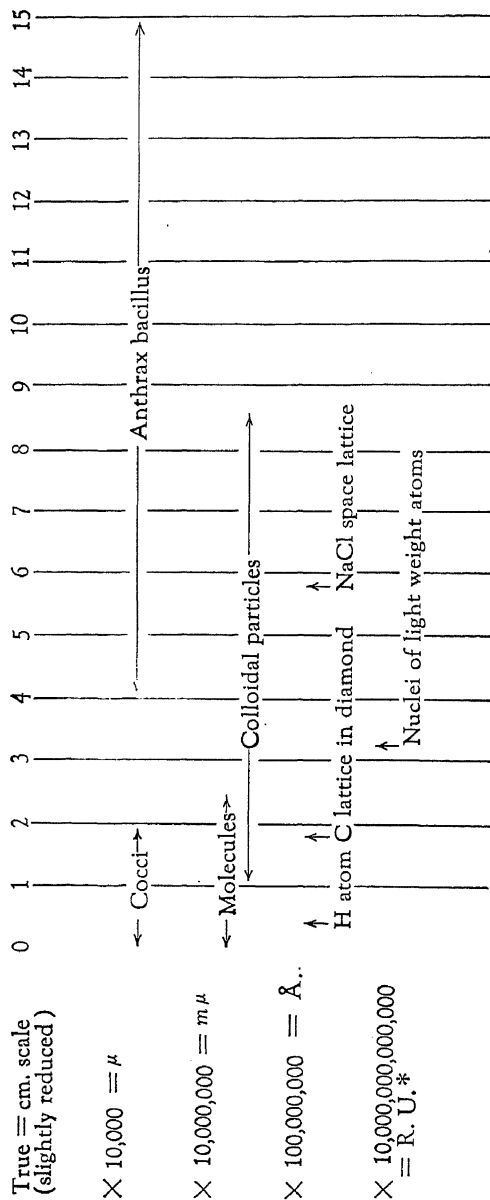
$$1\mu = \frac{1}{1,000} \text{ mm.}; 1m\mu = \frac{1}{1,000}\mu$$

TABLE VII

0.1 m $\mu$	1 m $\mu$	10 m $\mu$	100 m $\mu$	1 $\mu$	10 $\mu$	100 $\mu$	1 mm.
ULTRAMICROSCOPIC FIELD				MICROSCOPIC FIELD			
Particles visible but not resolvable Quartz no longer settles				Particles visible and resolvable Quartz settles			
Oil emulsion forms no cream layer				Oil emulsion forms a cream layer			
Particles pass through filter paper				Particles retained by filter paper			
Particles move very quickly				Brownian Movement not visible			
Crystalloid : Colloidal Dispersions : Dispersions				Suspensions			
"Cloudy solutions"							

TABLE VIII

CHART SHOWING SIZES OF VARIOUS UNITS AT VARIOUS MAGNIFICATIONS



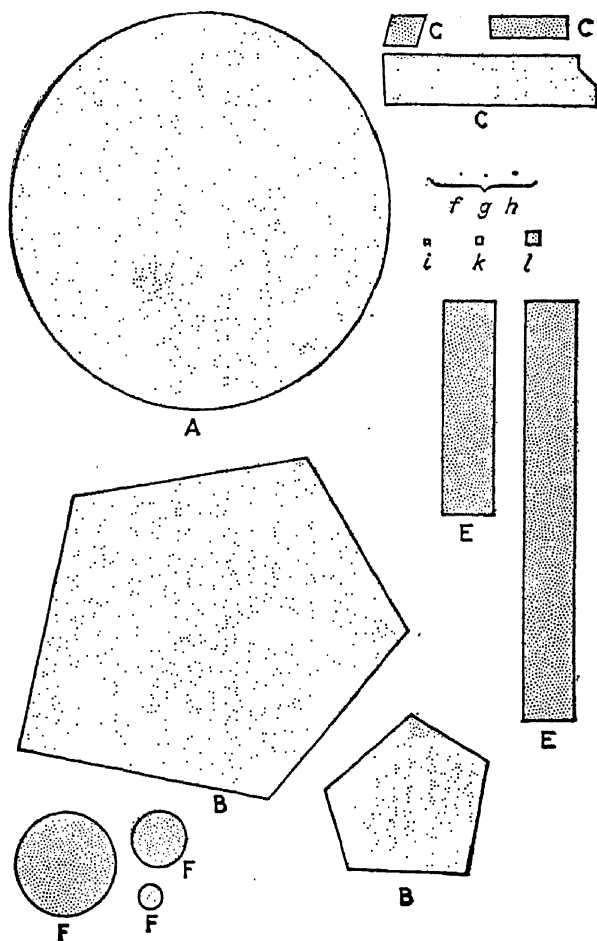
\* In dealing with the extremely minute sizes involved in describing nuclear diameters, it is convenient to use a unit of measurement one million times smaller than  $1 m\mu$ . This I have termed a "Rutherford Unit" (R.U.), and therefore  $1 \text{ R. U.} = \frac{1}{100,000} \text{\AA.} = \frac{1}{1,000,000} m\mu$ .

From Alexander, Vol. 1, p. 15.

$1 \text{\AA. (or A. U., Angstrom Unit)} = \frac{1}{10} m\mu$

TABLE IX

LINEAR MAGNIFICATION 1:10,000

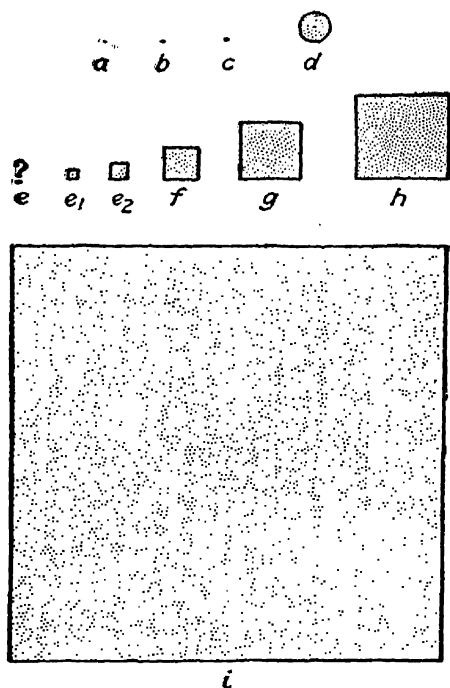


- A.* Human blood corpuscles (diameter  $7.5 \mu$ , thickness  $1.6 \mu$ ).  
*B.* Fragment of rice starch granule (according to v. Höhnelt)  $3-8 \mu$ .  
*C.* Particles in a kaolin suspension.  
*E.* Anthrax bacillus (length  $4-15 \mu$ , width about  $1 \mu$ ).  
*F.* Cocci (diameter about  $0.5-1 \mu$ , rarely  $2 \mu$ ).  
*f, g, h.* Particles of colloidal gold solutions  $Au_{732}$ ,  $Au_{92}$ ,  $Au_{97}$  ( $0.006-0.015 \mu$ ).  
*i, k, l.* Particles from settled gold suspensions ( $0.075-0.2 \mu$ ).



TABLE X

LINEAR MAGNIFICATION 1:1,000,000

a-d.—*Estimated Molecular Dimensions*

- a. Hydrogen molecule—dia. 0.1  $m\mu$ .  
 b. Alcohol molecule—dia. 0.5  $m\mu$ .  
 c. Chloroform molecule—dia. 0.8  $m\mu$ .  
 d. Molecule of soluble starch—dia. about 5  $m\mu$ .

e-h.—*Gold Particles in Colloidal Gold Solutions*

- e. Gold particle in  $Au_{16}$  (too small to determine).  
 e<sub>1</sub>. " " " " , about 1.7  $m\mu$ .  
 e<sub>2</sub>. " " " " , 3.0  $m\mu$ .  
 f. " " "  $Au_{73a}$ , " 6  $m\mu$ .  
 g. " " "  $Au_{92}$ , " 10  $m\mu$ .  
 h. " " "  $Au_{97}$ , " 15  $m\mu$ .  
 i. Gold particle in settled gold suspension.

## CHAPTER VI

### OPTICAL PROPERTIES OF COLLOIDS— THE ULTRAMICROSCOPE

As THE ultramicroscope revolutionized colloid research, a brief description of it is essential.

It is a matter of every-day experience that the unseen motes and dust particles in the air become visible in a beam of bright light, especially against a dark ground, and in this simple fact lies the principle of the ultra-microscope.

Faraday and later Tyndall made use of a convergent beam of light to demonstrate the optical inhomogeneity of solutions; for in fluids not optically clear, the path of the beam becomes more or less distinctly visible, because of the light scattered by the particles present. In this manner can be recognized much smaller quantities of matter than by spectrum analysis—in fact less than  $10^{-8}$  mg. (1/10,000,000) of metallic gold can thus be detected with the naked eye.

Prof. Richard Zsigmondy (University of Goettingen, Nobel Laureate) while experimenting with colloidal solutions conceived the idea of examining this light cone microscopically. His preliminary experiments having demonstrated that he could thus see the individual particles in various hydrosols, he sought the assistance of Dr. H. Siedentopf, scientific director of the Zeiss factory, in Jena, where was produced the first efficient ultramicroscope.

The ultramicroscope consists essentially of a compound microscope arranged for examining in a dark field an intense convergent beam of light cast within or upon the substance under examination. The light seen by the eye represents, therefore, the light diffracted, scattered or reflected upward by the substance or by particles within it.\*

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\* If a gas, a liquid, a crystal, or an "amorphous" solid be intensely illuminated by monochromatic light, a certain amount of the light is scattered or diffracted. The light, so scattered, passed through a spectroscope at right angles to the source of

If within a thin beam of light from a projection lantern we scatter successively powders of different substances in various degrees of fineness (mica ground to pass 60, 100 and 160 mesh; lampblack; powdered oxide of zinc; flake and powdered graphite), some of them will produce only a homogeneous illumination of the beam in which no isolated particles can be seen, whereas with others, the individual particles are distinctly visible.

Passing the beam through a beaker of distilled water, nothing can be seen; but upon the addition of a few drops of colloidal gold solution, which appears quite clear to transmitted light, the path of the beam through the fluid immediately becomes visible. This Tyndall effect,\* as it is called, might be considered a criterion of colloidal solution were it not that very minute traces of colloidal impurities can produce it and it is often exhibited by solutions generally regarded as crystalloidal—those of many dye-stuffs for example; furthermore with increasing fineness of subdivision the Tyndall effect decreases, disappearing as molecular dimensions are approached.

Just as in the cosmic field our most powerful telescopes fail to resolve the fixed stars, which are nevertheless *visible* as points of light of varying brilliancy, so, too, in the ultramicroscopic field, we can *see* particles much smaller than the resolving power of the microscope (that is, smaller than a wave length of light) provided only that they diffract sufficient light to affect the retina. Based upon the experience of astronomers we may be able greatly to increase the sensitiveness of the ultramicroscope by fortifying the eye, so to speak, with the photographic plate, using at the same time tropical sunlight or ultraviolet † light for illumination.

In the original form of the ultramicroscope, as perfected by Siedentopf and Zsigmondy, which is the one best adapted for the examination of transparent solids, a side illumination is affected

illumination, gives a photograph showing lines characteristic of the substance, and known as the Raman lines or Raman spectrum, after the discoverer, Sir C. V. Raman (University of Calcutta, Nobel Laureate). For details regarding this Raman effect and its utility, special books and articles must be consulted. It was predicted by Smekel in 1923, and discovered in 1928.

\* Also known as the Faraday-Tyndall effect. It is commonly shown by every searchlight at night, and when the sun "draws water" or throws a beam of light into a partly darkened room, the observer looking across the beam.

† This was done by The Svedberg (University of Upsala, Nobel Laureate).

by a microscope objective with micrometer movements, which throws an intense but minute conical beam of light into the fluid contained in a little cell having quartz windows at the front and top. Above this cell a compound microscope is adjusted vertically, so that the narrowest part of the light cone occupies the center of the focal plane. If the fluid under examination is optically clear or if it contains particles so small that they cannot diffract sufficient light to create a visual impression, the light cone cannot be seen. If enough light is diffracted, the light cone becomes visible, being homogeneous if the particles are too small or too close together to be individually seen, and heterogeneous if the particles can be individually distinguished. Particles or dimensions beyond the resolving power of the microscope (about  $\frac{1}{4}\mu$ ) are for brevity termed *ultramicros*. Ultramicros that can individually be made visible are called *submicros* (or hypomicros) while those so small that they produce an unresolvable light cone are termed *amicros*.

Small primary colloidal particles Zsigmondy terms "*protones*." If protones aggregate they yield secondary colloidal particles or "*polyones*."

Knowing the percentage of gold present in a colloidal gold solution and assuming a certain specific gravity and uniform shape for the gold particles, the average size and mass of a single particle of colloidal gold can be calculated, if the number present in a given volume be first counted. In this manner Zsigmondy has shown that the smallest particles of colloidal gold which can be individually distinguished with bright sunlight are approximately  $5\mu\mu$  in diameter, that is, five millionths of a millimeter; still smaller particles exist but they produce only an unresolvable light cone. Magnified 1,000,000 times such a tiny gold particle would be about  $\frac{1}{4}$  inch in diameter, while a human red blood corpuscle would be about 25 feet across, and a hydrogen molecule a speck barely visible. The gold particles in the unresolvable light cone must therefore closely approach molecular dimensions. In fact, by allowing amicros to grow into visibility in a suitable solution and then counting them, Zsigmondy has shown that some of the particles of colloidal gold have a mass of  $1-5.10^{-16}$  mg., indicating a size of 1.7 to  $3\mu\mu$ .

Various other types of ultramicroscopes, mainly modifications of dark field illumination, have been developed by Cotton and Mouton, Ignatowski (made by Leitz), Siedentopf (cardioid condenser, made by Zeiss) and others, and besides being useful in examining colloidal solutions, they have enabled pathologists to see and discover ultramicroscopic bacteria. Bausch & Lomb Optical Co. of Rochester, N. Y., are now producing useful ultramicroscopes.

To keep in touch with the advances in the field of instruments, the reader should consult the most recent catalogs of responsible manufacturers. Modern books on microscopy, *e.g.*, Chamot and Mason, contain sections on ultramicroscopes and their uses.

## CHAPTER VII

### DETERMINATION OF THE SIZE AND MASS OF COLLOIDAL PARTICLES

QUITE a number of methods of estimating the size and mass of colloidal particles have been suggested and tried, and several of these are referred to in more or less detail in various parts of this book. In evaluating the accuracy of the various methods, one must take into consideration the assumptions on which they are based. There is not room here for the details of each method, for which original papers or specialized publications must be consulted.

Dr. Alfred Kuhn (*Kolloid-Zeit.*, 1927, 38, 365-77) discussed the following methods for determination of particle size:

#### *A. Kinetic and Mechanical Methods*

- (1) Velocity of fall (mainly according to Stokes' Law; see p. 128).
- (2) Calculation from A. Einstein's formula for the diffusion constant

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \cdot \frac{cm^2}{sec.}, \text{ from which } r = 1.58 \cdot 10^{-8} \cdot \frac{1}{D}$$

- (3) Sedimentation equilibrium, as described by A. Westgren, (1915) in his Doctor's Dissertation, University of Upsala, Sweden.
- (4) Calculation based on A. Einstein's equation for Brownian motion

$$\bar{\Delta}^2 = \frac{RT}{N} \cdot \frac{t}{3\pi\eta r}, \text{ whence } r = 3.7 \cdot 10^{-13} \cdot \frac{t}{\bar{\Delta}^2}$$

- (5) Calculation from the osmotic pressure formula

$$P = RTn, \text{ whence the number of particles, } n = \frac{P}{RT}$$

Chemical analysis will show what quantity of substance is divided up into  $n$  particles.

- (6) Ultrafiltration (see papers and books of Prof. H. Bechhold, University of Frankfurt; also see p. 125).
- (7) Dialysis (subject to greater errors than ultrafiltration).
- (8) Calculation from the so-called "electro-viscous effect," based on the Einstein-Hatshek formula relating viscosity and conductivity.

$$\eta_s = \eta_o \left( 1 + 2.5 \varphi \left[ 1 + \frac{1}{\lambda \cdot \eta \cdot r^2} \left( \frac{\psi}{2\pi} \right)^2 \right] \right)$$

where  $\lambda$  is specific conductivity,  $\psi$  is the electrical P.D. of the double layer, and  $\varphi$  is the total volume of the particles.

### B. Optical Methods

- (9) Microscopical count, following chemical enlargement (see Westgren, *loc. cit.*). Zsigmondy developed the "nucleus" method for making gold sols (*Zeit. phys. Chem.*, 1906, 56, 65; "Kolloid-chemie," 3rd and 4th ed.; "Das Kolloid Gold," Dresden, 1925, p. 59 *et seq.*). Bechhold photographed ultrafilterable viruses after gold-plating them.
- (10) Direct count in the ultramicroscope. If  $m$  represents the mass of colloidal substance;  $s$ , its specific gravity; and  $n$  the number of particles into which this mass is dispersed, the following formula gives the value of the edge of a cube representing one particle

$$l = \sqrt[3]{\frac{m}{s \cdot n}}$$

If spherical particles are assumed, the sphere radius is

$$r = \sqrt[3]{\frac{3m}{4\pi \cdot s \cdot n}}$$

These formulae are based on certain assumptions, which are seldom, if ever, met in practice; (1) the particles are supposed to be of uniform size; (2) all of the dispersed substance should be

counted in (generally, some is amicroscopic, and unseen); the density is assumed to remain unchanged; cubic or spherical shape is assumed but is seldom correct; degree of dispersion must be unaffected by the dilution essential to accurate count (many hundred fields must be counted). The results are therefore only approximate and in each case the obvious errors must be considered. (See Zsigmondy, "Colloids and the Ultramicroscope" (1909), p. 117; also Chamot and Mason, "Handbook of Chemical Microscopy" (1930), Vol. I).

- (11) Ultramicroscopic measurement of the mean distance between the particles. If this be designated by  $d$ , then

$$1 = \sqrt[3]{\frac{m}{s}} \cdot d$$

- (12) Calculation from measurement of the intensity of diffracted light ( $I$ ) by Lord Rayleigh's formula

$$I = k \cdot \frac{n \cdot v^2}{\lambda^4}$$

where  $v$  is the particle volume,  $\lambda$  is the wavelength of the light used,  $n$  is the number of particles, and  $k$  is a constant. (See, *e.g.*, Svedberg, "Colloid Chemistry" (1924), p. 156 *et seq.*)

- (13) Calculation from X-ray data, based on the fact that with crystalline particles less than  $10^{-6}$  cm in diameter, the diffraction lines become broader. Debye and Scherrer developed the following formula:

$$\frac{1}{\cos \theta / 2} + b$$

where  $B$  is the angular breadth of a diffraction halo measured between points of half-maximum intensity;  $\theta$  is the diffraction angle;  $\lambda$  the wavelength used;  $D$  is the average thickness of the crystal parallel to a cubic axis; and  $b$  is the minimum breadth fixed by the particular apparatus. (See Prof. Geo. L. Clark, "Applied X-rays".)



S. R. Carter and B. R. Record (University of Birmingham) recently reported determinations of particle size of polysaccharides by measurements of osmotic pressure (see British Assn. Rept, 1935, p. 359; Chemistry and Industry, 1936, 55, 218). They used mainly methylated and acetylated derivatives of the carbohydrates, dissolved in organic solvents, *e.g.*, chloroform, and employed semipermeable membranes of "Cellophane" or "Viscocelle," adjusted for porosity by immersion in alcohol-water mixtures. The concentration of the solutions were determined by weighing on a micro-balance, following evaporation.

Methylated and acetylated inulin in chloroform gave particle weights of 6,300 and 8,900 respectively, indicating a chain length of 31 hexose units, which corresponds exactly with the values fixed by the "chemical" or "end-group" method. Glycogen from rabbit, haddock, hake and dog-fish, methylated and dissolved in nitromethane or in carbon tetrachloride, showed particle sizes varying from 3,400 to 5,400 units; acetylated glycogens in chloroform showed 5,900 to 17,000 units. These values are much higher than the chain length of 14 units indicated by chemical and by viscosity methods. Mr. Carter informs me that in the latter class of compounds there appears to be an association of the polysaccharide molecules into larger aggregates (probably of a zig-zag or spiral nature), which accords with the views of Haworth, Hirst, and their collaborators. (See p. 315.)

## CHAPTER VIII

### GENERAL PROPERTIES OF COLLOIDS

THE OPTICAL properties of colloids have been already referred to, as well as their simulation of chemical compounds. The other main general properties of colloids may now be considered under the following heads:

#### 1. *Interfacial Effects*

- (a) Surface and Interfacial Tension. The Parachor.
- (b) Wetting Power and Spreading.
- (c) Adsorption and Surface Concentration.
- (d) Residual Affinities and Molecular Assemblage; Cohesion; Adhesion; Crystallization; Mesomorphic States; Molecular Orientation; Dipoles and Dipole Moment.
- (e) Emulsions and Emulsification.

#### 2. *Electrical Effects*

- (a) Electric Charge Patterns.
- (b) Helmholtz and Gouy Layers.
- (c) Epsilon and Zeta Potentials.
- (d) Electro-kinetic Effects—Endosmosis, Cataphoresis, Streaming Potential, Migration Potential.

#### 3. *Diffusion Effects*

- (a) Diffusion and Differential Diffusion.
- (b) Dialysis and Electrodialysis.
- (c) Osmosis, Electro-osmosis, and Osmotic Pressure.
- (d) Donnan's Equilibrium.

#### 4. *Separations*

- (a) Ultrafiltration and Electro-ultrafiltration.
- (b) Sedimentation.
- (c) Ultracentrifugation.

#### 5. *Sols and Gels*

- (a) Peptization and Pectization (Dispersion and Coagulation).

- (b) Viscosity, Fluidity, Plasticity, Mobility.
- (c) Thixotropy.
- (d) Ageing.

6. *Swelling and Shrinking*

Hysteresis.

7. *Colloidal Protection*

- (a) Historical and Descriptive—Gold Number.
- (b) Double or Plural Protection.
- (c) Autoprotection.
- (d) Cumulative Protection.

1. INTERFACIAL EFFECTS

SURFACE AND INTERFACIAL TENSION

The volume (and weight) of a drop of a liquid is so uniform, under uniform ordinary conditions, that medicines of various kinds are commonly prescribed to be taken in doses of so and so many drops. This does not mean, however, that drops of different kinds of liquids are alike in volume. By dropping alcohol, water, mucilage, mercury, and other liquids from the same medicine dropper, it will be seen that the drops of water are larger than those of alcohol, while mucilage gives still larger drops. If a definite number of drops of each liquid is collected in the same small measuring tube, it will be seen that the volumes differ considerably. So do the weights of the drops.

Why is this?

By making the drops form slowly, we see that they hold together, just *as if* they were surrounded by an invisible, flexible, distensible skin or bag. As the growing drop becomes heavier and heavier, the "skin" tears near the dropper tip, but instantly heals itself up to make a new bag bottom for the next drop. Meanwhile, the torn top of the "bag" surrounding the falling drop, has instantaneously closed itself to round out a sphere. This "skin" or "bag" effect is consequent upon the fact that the molecules at the outside are situated quite differently from those on the interior of the drop. The inside molecules are surrounded equally on all sides by their fellows, while the molecules in the surface film have only the relatively slight attraction of the air

on the outside, and therefore huddle together toward the center of the drop, giving the *effect* of a surface skin. It is, however, not a real skin such as, *e.g.*, forms on bubbles of soap-bark or saponin solutions; for when these bubbles are collapsed, the saponin skin wrinkles up and remains even after the bubble is gone, like the grin of the Cheshire cat. The boundary layer of a drop of pure water or alcohol, on the other hand, consists of transient molecules passing in and out of the interface. As Prof. N. K. Adam (Cambridge University) says ("The Physics and Chemistry of Surfaces," 1930, p. 30): "The surface pressure is the tangible, physical force; the surface tension merely the mathematical equivalent of the free surface energy."

Naturally, the specific gravity of the liquid (weight per unit volume) enters into our calculation, for the *weight* of a drop is what causes it to tear loose. If we *weigh* a definite number of drops, or *count* the number of drops given by a definite weight or volume of a liquid, we can calculate the surface tension.\* A carefully made dropper which enables us to count the exact number of drops given by a definite volume of liquid is called a stalagmometer or *drop-measurer* (Traube) or a *tonometer* (Kopaczewski).

Strictly speaking, the *surface tension* of a liquid is the force exerted at right angles across a line of unit length on the surface of the liquid, when it is in contact only with its own vapor. Where other molecules are present in the interface, as is almost invariably the case, what is measured in the *interfacial tension* of the liquid with the surrounding matter. According to T. W. Richards (Harvard University, Nobel Laureate) and E. K. Carver (J. Am. Chem. Soc., 1921, 43, 827-47), in the presence of air the true surface tension does not differ from the interfacial tension as determined, by more than 0.5% in most cases.

Since the attraction between the exterior medium (air, in the cases we have been considering) and the material composing the drop, is a factor in determining the strength of the interfacial layer (that is, the interfacial tension), it stands to reason that we must always specify *against* what medium the "surface ten-

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\* For detailed treatment of surface tension, see Alexander's "Colloid Chemistry, Theoretical and Applied," Vol. I (Chemical Catalog Co., 1926), especially the papers of Prof. Wm. D. Harkins and of Sir Wm. B. Hardy; also "Physico-chemical Methods," by J. Reilly and W. N. Rae, D. Van Nostrand Co., 1932.

sion" is measured. This can be readily shown by simple experiments. Thus when mercury is spilled, it tends to form a multitude of tiny globules, which have such a high surface tension against air, that they do not readily cohere and run together. Sir C. V. Boys has pointed out (*Nature*, 1934, 134, 29) that mercury spilled on a smooth surface (*e.g.*, a cork floor) may be easily gathered up if the floor is sprinkled with water from a wash-bottle, and the mercury droplets "swept up" with a squeegee or a bit of stiff cardboard. The surface tension of the mercury against water is so much less than against air, that the droplets fuse into one big mass—the quicksilver becomes less "quick".

If a drop of butter or fat be placed on a cup of hot water, it floats as a spheroid (a sphere flattened by weight of the drop) because the attraction between the fat particles for each other exceeds the attraction of the water surface for the fat. If we now increase the attraction between the fat and the water by dissolving some soap in the water, the conditions are reversed; the fat is dragged out into a thin skin on the surface of the water and upon slight agitation goes into a fine dispersion or emulsion. We have made oil and water mix, contrary to the old saw which says they won't.

From this it is obvious that if two substances have a low surface tension against each other, they will tend to "wet" each other. Water won't wet oil—until we add soap to reduce their interfacial tension. That is why soap and alkalis make water wet greasy dishes, and emulsify the grease. Alkalis form some soap from the fat or from the free fatty acid usually present in the fat.

If we dip a perfectly clean capillary glass tube into water, the water will wet the interior of the capillary, and surface tension will drag a column of water to a considerable height in the capillary, and support it there. From the height of the "capillary rise," at equilibrium, the surface tension water/air may be calculated.\*

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\* The general formula is

$$\gamma = \frac{1}{2} r h g d$$

where  $\gamma$  is the surface tension;  $r$ , the diameter of the capillary;  $h$ , the capillary rise;  $g$  the force of gravity (a constant, 980); and  $d$ , the density of the liquid (in this case, water, for which  $d = 1$ ). For exact details, see Harkins' paper, *lib. cit.*, p. 246.

*The Parachor:*

D. B. McLeod (Trans. Faraday Soc., 1923, 19, 38) found *empirically* a relation connecting density and surface tension in liquids. If  $D$  is the density of a liquid and  $d$  the density of its vapor, McLeod found that  $\frac{\gamma}{(D-d)^4} = C$ , where  $\gamma$  is the surface tension, and  $C$  a constant, different for each liquid.

Prof. S. Sugden (University of London) found (J. Chem. Soc., 1924, 125, 1177, and subsequent volumes) in McLeod's equation a basis for comparing molecular volumes at some definite surface tension, chosen as standard; for then the effect of the thermal agitation of the molecules is absorbed in the surface tension, and thus neutralized and eliminated as a factor.

If we take the fourth root of the above equation and multiply both sides by the molecular weight,  $M$ , we get

$$\frac{M}{D-d} \gamma^{1/4} = M C^{1/4} = P, \text{ called by Sugden the } \textit{parachor}.$$

By taking the surface tension at a low temperature, far removed from the "critical point" (where the vapor density would be large),  $d$  may be neglected, and the equation becomes  $P = \frac{M}{D} \gamma^{1/4}$ , where  $\frac{M}{D}$  is the molecular volume, independent of temperature.

Sugden found that by means of his formula he could calculate the value of the parachor ( $P$ ) from the chemical composition, in the case of a large number of chemical compounds, with an accuracy of within 2% in 145 cases and within 1% in 104 cases. With simple molecules, the parachors are equal to the sum of the parachors of the constituent atoms, being thus *additive*. Where multiple bonds or ring structures exist, however, certain constants must be added to the parachors, to allow for deviations due to molecular structure; the parachors then become *constitutive*. Consequently, where the structure of a compound is not yet known, we have means for judging whether its structure is simple or whether it has double bonds or rings. Adam states (*lib. cit.*, p. 165) that through parachors, compounds are compared under what amounts to "equal degrees of self-compression by the intermolecular cohesive forces." For fuller discussion, see Chapter II on The Parachor in "Recent Advances in Physical

Chemistry" (P. Blakiston's Son & Co., 1933) by S. Glasstone (Sheffield University).

### THE SPREADING OF LIQUIDS OR "WETTING POWER"

The ability of liquids to wet solids and to spread on the surface of other liquids is a dominant factor in a great number of important natural and industrial processes, *e.g.*, in living organisms, in agriculture, washing, painting, printing, water-proofing, flotation of ores, etc.

Consider a drop of liquid (*e.g.*, oil), L, floating on water (see Fig 2). The rim of the drop at the air/water interface is subject to three pulls:

(1) The surface tension water/air ( $\sigma_{W/A}$ ) which tends to drag out the rim and make the drop flatter and flatter;

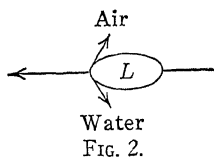


FIG. 2.

(2) and (3) The surface tensions liquid/air ( $\sigma_{L/A}$ ) and liquid/water ( $\sigma_{L/W}$ ), which tend to pull the rim in and make the drop rounder and rounder.

What happens in any particular case depends on the balance between these three pulls. Spreading will tend to occur if the air/water surface tension dominates or balances the other two pulls, which very often happens because water has a high surface tension against air. Expressed in a concise form or formula:

If  $\sigma_{W/A} \geq \sigma_{L/A} + \sigma_{L/W}$ , spreading tends to occur.

If  $\sigma_{W/A} < \sigma_{L/A} + \sigma_{L/W}$ , the liquid tends to form a drop resting on the surface of the water, *e.g.*, like a drop of castor oil.

But there are other possibilities. Suppose that the liquid is completely miscible with the water. Then  $\sigma_{L/W}$  is a dynamic surface tension, proceeding toward zero; and we would expect spreading if  $\sigma_{W/A} > \sigma_{L/A}$ ; that is, if two liquids are completely miscible, the one having the smaller surface tension will spread over the one with the larger surface tension. This permits the detection of very small differences of surface tension, for a warmer liquid spreads over the surface of a colder body of the *same*

*liquid*, even though they may quickly mix. Reference may here be made to the remarkable instantaneous photographs taken fractions of a second apart, showing what happens when drops of one liquid fall into another. This work of Lord Rayleigh should be supplemented by "slow movies" taken by modern methods, whereby upwards of 40,000 pictures per second can be taken, and then projected at the rate of about 20 per second.

Furthermore, in a great many cases, bringing the two liquids together may result in great changes in the various surface tensions involved. Small amounts of the liquid (L) or even of its vapor, may so lower the surface tension of the water (*e.g.*, as with benzene, chloroform) that the drop will not spread. On the other hand, the liquid may continue to dissolve in the water, until the solubility limit is reached; whereupon the surface ten-

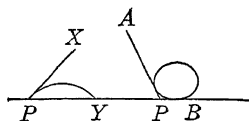


FIG. 3.

sion of the aqueous solution against the air becomes so much lowered, that the liquid forms a layer above it, as is the case with ethyl ether, for example.

Naturally, anything that lowers the surface tension *between the liquid and water*, will tend to facilitate spreading. Thus a pure petroleum oil with  $\sigma_{w/L} = 48.3$  formed a lens on water; but when mastic was added to the oil so that its  $\sigma_{w/L} = 16.3$ , it spread rapidly.

*Solid/Liquid; Angle of Contact; Displacement of One Liquid by Another.* When a drop of liquid is placed on a solid surface, we have three possibilities:

(1) Wetting may not occur, as is the case of water drops on waxed or smoked metal surfaces, on cabbage leaves, or on a duck's back.

(2) Complete wetting may occur, as when kerosene wets iron.

(3) The drop of liquid may remain intact on the solid surface, like water on iron, forming an *angle of contact*  $\theta$ , as indicated in Fig. 3. Obviously complete wetting occurs when the



angle of contact ( $\theta$ ) is zero, whereas in the opposite limiting case, no wetting occurs if the angle of contact is  $180^\circ$ . In case (3) only portion of the surface tension liquid/air is operative, the amount being proportional to the *cosine* of the contact angle. Consequently, the balance in the forces affecting the rim of the standing drop is expressed as follows:

$$\sigma_{\text{SOLID/AIR}} = \sigma_{\text{FLUID/AIR}} \cos \theta + \sigma_{\text{SOLID/FLUID}},$$

$$\text{or } \sigma_{\text{S/A}} - \sigma_{\text{S/F}} = \sigma_{\text{F/A}} \cos \theta$$

The difference between the interfacial tensions of the solid (against air and the fluid, respectively) is termed by Freundlich the *adhesion tension*.

Often the phenomenon of wetting involves the competition of two liquids for the surface of a solid, instead of competition between a liquid and a gas. Depending on the way the surface forces happen to balance, a powder will pass into one or the other of two immiscible liquids, or may remain in the interface between them.

Among the many experiments in this field, are those of F. B. Hofmann (Z. physik. Chem., 1913, 83, 385) who found that glass and gypsum were always passed preferentially into the water, when water was layered with organic liquids such as chloroform, xylene, or petroleum oil. Sulphides ( $\text{MoS}_2$ , Pbs,  $\text{HgS}$ ), oxides ( $\text{Fe}_2\text{O}_3$ ,  $\text{HgO}$ ), halides ( $\text{AgI}$ ,  $\text{PbI}_2$ ,  $\text{HgI}_2$ ), and carbon in all cases remained more or less in the interface. Time enters as a factor in these surface displacements. Thus, if some petroleum is poured into a clean-air-dry test tube, and some water poured in promptly thereafter, the water will displace the petroleum in a few seconds because the oil has not yet had time to displace the air film, which water readily does. If we wait a few minutes before adding the water, the oil displaces the air, and the water then has the more time-consuming task of displacing the oil film.

Gossart (Ann. de chim. et de phys., 1895, (5), 4, 391) pointed out that where a drop of liquid dances about a liquid surface (as is often seen in filtration, in titration, or in rowing, when splashing occurs), a film of adsorbed air is what temporarily prevents the taking up of the drop. He found that *gliding drops* of this kind appear only when the drop and the liquid are chem-

ically alike, for then the air film is not readily dissolved away. It is claimed that by dropping a solution onto the surface of another of like chemical nature in which proportions are progressively varied, the appearance of gliding drops will announce their approximate identity. (See H. Freundlich, "Colloid and Capillary Chemistry," Hatfield's trans., p. 101.)

In making a daguerreotype, the earliest form of photography, a cleaned and polished silver plate is coated with a layer of silver iodide by exposure to iodine vapor (usually some bromide is formed by adding bromine, so as to make the surface more sensitive). After exposure, the plate is subjected to mercury vapor, which does not wet the unexposed silver iodide, but which condenses preferentially on the exposed areas where there is colloidal silver, the amount of deposition being proportional to the extent of the light effect. The unaffected iodide is then dissolved out by sodium hyposulphite, leaving the amalgam image.

A very direct and practical approach to the problem of wetting was made by Prof. W. D. Harkins (University of Chicago) and his co-workers (J. Am. Chem. Soc. 1917 *et seq.*; also Alexander's "Colloid Chemistry, Theoretical and Applied," Vol. I, p. 227) on thermodynamic principles.

If a liquid  $b$  spreads out over a liquid  $a$ , the surface of  $a$  is covered over and disappears. Assuming that the surface film of  $b$  does not dissolve in  $a$ , there are formed two new surfaces: (1) the new interface  $ab$  and (2) the free top surface  $b$ . The amount of free energy used in this operation, termed the *spreading coefficient* and represented by the symbol  $S$ , is evidently the difference between the free energy of the initial surface of  $a$ , which we will call  $\gamma_a$ , and the free energies of the two final surfaces, which we will call  $\gamma_b$  and  $\gamma_{ab}$ . Expressing this in a concise form or formula, we have

$$S = \gamma_a - (\gamma_b + \gamma_{ab}) = \gamma_a - \gamma_b - \gamma_{ab} \quad (1)$$

Now the *work of adhesion* ( $W_A$ ) between the two liquids (that is, the work necessary to pull apart 1 sq. cm. of the interface  $ab$ ), is fixed by the fact that, with the break, the interface  $ab$  vanishes and is replaced by the two new surfaces  $a$  and  $b$ . Therefore

$$W_A = \gamma_a + \gamma_b - \gamma_{ab} \quad (2)$$

But the *work of cohesion* of the spreading liquid  $b$  (that is, its resistance to being dragged out), which we will represent by the symbol  $W_c$ , can be measured by the work required to pull apart a bar of  $b$  having a cross section of 1 sq. cm., thereby forming *two* new surfaces each with the free energy  $\gamma_b$ . That is,

$$W_c = 2\gamma_b \quad (3)$$

Subtracting Equation (3) from Equation (2), we get  $W_A - W_c = \gamma_a - \gamma_b - \gamma_{ab}$ . And as this last term =  $S$ , we have  $S = W_A - W_c$ .

Expressed practically, this means that if the attraction of the surface of  $a$  for  $b$ , overcomes the power of  $b$  to hold together, then  $b$  will spread on  $a$ . Quite obviously, if  $b$  spreads readily on  $a$ , we should expect that  $a$  would not spread on  $b$ ; for a high surface energy of  $a$  would then work against spreading instead of in favor of it as in the first case. Therefore most organic liquids spread on water, while water will spread on very few organic liquids, unless the interfacial tension is lowered by soap or the like.

### ADSORPTION AND SURFACE CONCENTRATION

*Surface Activity.* The apothecary C. Musculus in 1864 (Chem. Zentral-Bl., p. 922) found that while salts had comparatively little effect on the rise of water in a capillary tube (he called them *capillary inactive*), such substances as alcohol, acetic acid, bile, etc., markedly reduced the capillary rise (he called these *capillary active*). Twenty years later I. Traube revived this work, and investigated the surface tension of aqueous solutions of many common substances [Berichte, 1884, 17, 2295; J. prak. Chem., 1885 and 1886; Lieb. Annalen, 265, 27; also Alexander's "Colloid Chem.", Vol. I, p. 640 (Chem. Cat. Co., 1926)]. Traube found that many of the substances he tested, especially electrolytes, did not materially affect the surface tension (termed *surface inactive*), others produced marked changes in the surface tension, and were termed *surface active*. As is true with most classifications of natural phenomena, the line of demarcation between the two groups was not a sharp one, which, for instance, is also the case between electrolytes and non-electrolytes.

The residual affinities (see p. 88) residing in molecules, which necessitated the introduction of the well-known "cohesion factor,"  $a$ , in the equation of van der Waals, is responsible for the "attraction intensity" or "attraction pressure" which draws together the molecules of solute and solvent. Thus, with unstable hydrophobe colloids the attraction pressure is small. Traube considers this *intensity* factor to lie at the root of most surface phenomena, and points out that it is omitted from the Arrhenius equations which consider only the *capacity* factor, that is, the number of particles (see Traube *loc. cit.* Alexander, p. 645).

*Adsorption vs. Absorption.* It had long been known that certain porous substances, *e.g.*, charcoal, diatomaceous earth (kieselguhr), fullers' earth, etc., had the power of taking up and strongly holding gases and dissolved substances. This was originally spoken of as *absorption*, although this term was also applied to the drinking in, by capillarity, of liquids into the body of a substance; *e.g.*, of water by sponge, of ink by blotting paper. As far back as 1770 Joseph Priestley confirmed the observation communicated to him by F. Fontana that charcoal "absorbs" gases. For generations charcoal has been used to absorb odors and to remove color from liquids (*e.g.*, wine). Hunter pointed out the high value of coco-nut charcoal, and in 1874 Tait and Dewar used charcoal to produce extremely high vacua. Prof. James W. F. Johnson ("The Chemistry of Common Life," 2nd ed., 1879) described the charcoal respirator of Dr. J. Stenhouse (1854), useful as a protector against noxious gases.

It was found, however, that in many cases, substances could be rapidly fixed to apparently non-porous surfaces, and that a *reversible* equilibrium was established, that is, an equilibrium which could be reached equally well from higher or lower concentration levels, and that the fixed substance could be removed by repeated washing or lixiviation. This rapid and reversible fixation of substances at surfaces has been termed *adsorption*, even though in some cases it may be followed by chemical reaction or by a slower penetration of the *adsorbate* (adsorbed substance) into the *adsorbent* (adsorbing substance). Since it is often difficult to distinguish between absorption and adsorption, and their respective importance in a phenomenon, Prof. J. W. McBain (Stanford University) proposed the term *sorption* and

the verb *to sorb*, to include both. (Phil. Mag. 1909, (6), 18, 916.)

### *Gibbs' Adsorption Law*

J. Willard Gibbs (Conn. Acad. Sci., 1876, 3, 391) proved by thermodynamic calculation that if a dissolved substance lowers the surface tension of the solvent, the dissolved substance (or *solute*) tends to concentrate at the boundary layers or interfaces, because by this process the potential energy of the system strives toward a minimum. This is *positive* surface concentration or *positive adsorption*. On the other hand, substances which increase the interfacial tension are forced away from the interfaces, leading to diminution of their concentration there, that is, to *negative adsorption*.

As was pointed out by H. Freundlich ("Colloid and Capillary Chemistry," Hatfield's trans. 3rd ed., p. 50), molecules cannot rush in and out of surfaces without taking time for the operation, even though in many cases the time is inappreciable. Cumbersome molecules or molecular aggregates, however, do take an appreciable time to work their way to or from surfaces, and we can measure the variable *dynamic surface tensions* as the system works its way toward the final equilibrium, the *static surface tension*. (See, e.g., P. Lecomte du Noüy (Pasteur Institute, Paris) in Alexander, "Colloid Chemistry, Theoretical and Applied," Vol. I, and Edgard Zunz, in Vol. II).

*The Nature of Adsorption.* Is adsorption to be considered a chemical or a physical phenomenon? Because of the very great variations in the nature of adsorbents and in adsorbed substances, experimental evidence can be found to support both views, and the answer will depend upon what limitations we place on the meaning of the terms "chemical" and "physical". (See p. 23.)

The quantitative investigation of adsorption is not as simple as it might seem, because what are supposed to be the same adsorbents differ greatly at times in chemical and in physical structure (nature and percentage of impurities present, capillary cracks and interstices); furthermore the medium from which the adsorption is to be measured, as well as substances in it, may influence or interfere with the adsorption process, or obscure the true results. Thus "bone black" contains calcium, phosphate,

and other residual substances from the original bone. Wood charcoals generally contain alkalis. Blood charcoal has its own impurities, and even the extremely pure activated sugar charcoal prepared by Bartell and Miller (J. Am. Chem. Soc., 1922-24) from sugar (sucrose, re-crystallized) was shown to contain graphite.

*Adsorption Quantitatively Considered—Freundlich's  
Empirical Adsorption Isotherm*

Apart from the lack of purity and uniformity of the adsorbing surface, its precise *quantity* or area is generally not known. We are therefore compelled to figure the amount of substance adsorbed against the *weight* of the adsorbent. If we designate by  $a$  the *amount of gas adsorbed per gram* of charcoal at *any* pressure,  $p$ , then its relation to the amount ( $\alpha$ ) adsorbed by the same amount of charcoal at the *same temperature* but at *unit* pressure (1 cm. of mercury), is roughly expressed by what Freundlich (*lib. cit.*, p. 111) calls "*the empirical general parabolic equation*"

$$a = \alpha p^{\frac{1}{n}}$$

because when  $n$  equals 2 the equation is that of a parabola. However,  $n$  usually has values between about 1 and 5, so that the *adsorption exponent*  $\frac{1}{n}$  falls between 1 and 0.2.

This equation is known as *the adsorption isotherm*, because changes in temperature likewise influence adsorption, and it is therefore necessary to maintain *temperature constant*, while the pressure is varied. The results, when plotted on coordinate axes give a sweeping parabola; but if the adsorption isotherm is written in its logarithmic form

$$\log_{10} a = \log_{10} \alpha + \frac{1}{n} \log_{10} p$$

the results plot approximately as a straight line.

If a number of logarithmic adsorption lines are determined for the same substance but at *different* temperatures, they form a roughly parallel series or family of straight lines.

*Langmuir's Kinetic Treatment of Adsorption.* By considering adsorption of gases as an *equilibrium* between the velocity or rate of *fixation* of a gas at a unit surface and its rate of *evaporation* from the same area, Irving Langmuir (Nobel Laureate, J.A.C.S. 1916, 38, 2221; 1917, 39, 1885; 1918, 40, 1361) developed a formula expressing this kinetic balance, which agrees with many experimental data. It is questionable, however, if the formula can hold with adsorbed layers more than one molecule deep, or where (A. B. Lamb and A. S. Coolidge, Journal Am. Chem. Soc., 1920, 42, 1146) the adsorbed gas forms a liquid layer. Thus Langmuir points out (Alexander's "Colloid Chemistry, Theoretical and Applied," (1926), Vol. I, p. 531), that since the attractive force between molecules varies about inversely as the *ninth* power of the distance between them "the force acting at the near surface of the first molecule would be about 10,000 times as great as the further side of the molecule. We are then surely not justified in considering that the deformation would be the same as if the molecule were in a uniform field having the intensity of that at the center of the molecule." Langmuir further states (Chemical Reviews, 1930, 6, 468): "This principle of independent surface action (see also Colloid Symposium Monograph, 1925) will always be only an approximation to the truth, but there are many cases where it applies with sufficient accuracy and so greatly simplifies the problems of the interactions between molecules so complex that no solution is otherwise possible. Let us consider some of these problems.

"The theory of adsorption in monomolecular films on solids and liquids (J. Am. Chem. Soc., 1918) is an example of the application of this principle. According to this theory, the force which holds an adsorbed molecule or atom on a surface depends on the character of the surface of contact between the molecule and the solid. If a second layer of molecules should form, the forces holding the molecule to the second layer are thus entirely different from those holding the molecules of the first layer."

According to experiments of Prof. I. Traube (now at Univ. of Edinburgh; see Trans. Faraday Soc., 1935, 31, 1730-9), if the adsorbate is presented in very fine dispersion (*e.g.*, octyl alcohol, caprylic acid), "the degree of adsorption changes drastically and the Langmuir theory is no longer applicable, for 1,000

or more layers can be adsorbed in these cases. Even though an adsorbent such as diphenylamine does not adsorb single molecules (*e.g.*, of caprylic acid) out of an aqueous solution, it can adsorb large quantities of that substance, if it is not dissolved in water but is in the form of emulsified particles." Traube found that inactive charcoals are nearly or wholly as efficient as activated charcoals *for the adsorption of emulsified colloidal particles*. In such cases the parallelism between adsorption and surface activity as postulated by Gibbs' law breaks down; for here the adsorption is larger than corresponds to the surface activity, since single molecules diminish the surface tension of an aqueous solution relatively far more than when they are aggregated to submicrons.

In his Medal Address (J. Franklin Inst., 1934, 218, 143-171) Langmuir states that atoms of caesium adsorbed in a second layer on tungsten are held by forces so weak that they evaporate at room temperature about  $10^{36}$  times faster than those in the primary layer, which are able to increase the electron emission of the tungsten  $10^{26}$  times. The use of this fact in radio tubes is obvious.

In the case of mercury atoms condensing on a cool glass surface, quite another situation arises, because mercury atoms have a much greater attraction for each other than they have for glass. Consequently even before the primary layer is complete, second, third, and fourth layers begin to form, leading to the "mopping up" of molecules into nuclei which grow into droplets, or at low temperatures, into crystals of mercury. A similar effect is observable in a bottle containing at the bottom a small quantity of iodine or camphor crystals, which keep the air in the bottle saturated with vapor of the substances. The camphor crystals seem to form preferentially on the wall of the bottle turned *toward* the light (*positive photodromy*), while with iodine they form *away* from the light (*negative photodromy*).\* The phenomenon first reported and named by G. Quincke (Drude's Ann. der Physik., 1902, 7, p. 85) has been described by K. Schaum (Zeit. wissenschaft. Photographie, 1913, 12, 93-100), and deserves further study. The action of light also produced changes in the turbidity of the solutions of these substances, according to Schaum.

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\* From personal observations on this phenomenon it seems that slight temperature differences may be determinative of the surfaces where crystallization is favored.—J.A.



## RESIDUAL AFFINITIES AND MOLECULAR ASSEMBLAGE

If the attractive forces existing between atoms were entirely balanced or satisfied by their chemical combination, then every chemical compound would behave as a perfect gas so far as concerns the factor  $a$  in the equation of van der Waals. But in all chemical compounds there exist residual attractions or stray fields of force which exert a controlling influence on what are ordinarily termed the physical properties of the compound—its state (gaseous, liquid or solid), its crystallization, solubility, boiling point, conductivity for heat and electricity, dielectric constant, etc. This residual attraction is responsible for the phenomena we call *cohesion*, *adhesion*, *adsorption*, and *molecular orientation*, and its range of effective action (of the order of  $10^{-8}$  cm.) is much less than the diameter of a molecule.

*Cohesion.* The Standard Dictionary defines *cohesion* as “that force by which molecules of the same kind or of the same body are held together, so that the body resists being pulled to pieces. It is strong in solids, weak in liquids, and probably absent in gases. The distinction between *cohesion* and *adhesion*, once insisted upon strongly, is not now regarded as fundamental. Some physicists have limited *cohesion* to particles of the same kind, others to those of the same body. Thus the force that holds the mica to the feldspar in granite would be called *cohesion* by some, and *adhesion* by others.” Adhesion is defined as “a molecular force, or the result of it, by which certain bodies stick together.”

It would be better to say of *cohesion* that it is *negligible* in gases and *eludes measurement* in liquids. The internal pressure of water (about 14,000 atmospheres) indicates that liquids have great cohesion, but this is difficult to demonstrate or to measure because liquids flow. It was in the course of consideration of internal pressures that Prof. Theodore W. Richards (Harvard University; Nobel Laureate) chanced upon the following statement in the third edition of Sir Isaac Newton’s “Opticks” (see Chemical Reviews, 1925, 2, No. 3). “The parts of all homogeneous hard Bodies which fully touch each other, stick together very strongly . . . I . . . infer from their Cohesion, that their particles attract one another by some force, which in immediate contact is exceeding strong, at small distances performs the chymical Operations above mention’d, and reaches not far from the

particles with any sensible effect. . . . There are, therefore, Agents in Nature able to make the Particles of Bodies stick together by very strong Attractions. And it is the Business of experimental Philosophy to find them out."

A moment's consideration will show that *homogeneity* is purely relative, and that most of the things so spoken of are demonstrably *heterogeneous*. We have probed into the structure of atoms, and are now probing into atomic nuclei and the sub-atomic units. The cleavage of crystals along preferential planes is due to inhomogeneity in their constituents, and this is an outstanding phenomenon in mica.

A "perfect" crystal of rocksalt, where the sodium and chlorine atoms are regularly disposed in a cubic space lattice, would seem "homogeneous." But Joffé (Joffé, Kirpitsheva and Lewitzsky, *Zeit. Physik.*, 1924, 22, 286) observed that when such a crystal is subjected to tension, it shows only about a strength of 0.45 kg. per sq. mm, whereas calculation based on electrical theory demands about 200 kg. per sq. mm. If one end of the crystal was immersed in water, the crystal always broke, under tension, *outside* of the water, even when the submerged end was greatly reduced in diameter. It was concluded that the "perfect" crystal contained many imperfections. By chilling spheres of rocksalt in liquid air, and then immersing them in molten lead, Joffé demonstrated a strength exceeding 70 kg. per sq. mm.

Fibers and rods drawn from highly heated glass or silica showed great increase in strength and elasticity. Griffith found (*Phil. Trans.*, 1920, 221 A, 163) that a glass showed an increase in tensile strength from 17.5 kg. per sq. mm. to 222 kg. per sq. mm., and extrapolation to molecular diameters indicated a limiting strength of 715 kg. per sq. mm. The "strong" drawn state was unstable, reverting on scratching to the ordinary "weak" state. Drawn silica, though quite flexible, finally burst like a Prince Rupert drop, even the thick ends of the original rod being shattered by the elastic tremor, which reminds one of an explosive wave.

Griffiths also attributed the weakness of ordinary substances to the presence of large numbers of minute cracks, which, when tension is applied, result in extreme localization of internal stress. A web of cloth will support a considerable weight if the cloth is

so held that all of its constituent threads along the line of tension are simultaneously brought into play. The same cloth may be readily torn, especially if there is an initial starting "nick" or tear, because then in tearing we break only one or a few threads at a time. The trick of tearing a pack of cards or a telephone book involves manipulation so that only one or a few sheets are being initially torn at a time; for it is easier to continue a tear than to start one. These practical matters illustrate the old adage "In union there is strength."

But another aspect demands consideration.

If the cooling of hot-drawn quartz fibers is quick enough, the crystals tend to be of colloidal dimensions, so that few, if any, voids are formed. This is, of course, a metastable state, upset by scratching, or, as Griffith found, by merely ageing; whereupon the ordinary "weak" state is reached. The shattering "wave" observed when the quartz filament "exploded," may be understood as a sudden rush, unbalanced on one side, of exceedingly tiny crystals towards the lower potential condition of larger crystals, albeit that this latter condition when established would result in weakening voids. Furthermore, the formation of larger crystals is, in itself, a move towards weakness, because molecular or atomic attractions are weaker along some crystal planes than along others, and preferential cleavage would result.

A somewhat similar phenomena is found in sulfur. When heated to its second zone of fluidity (over about 200° C.) and then suddenly chilled, sulfur yields a tough transparent flexible mass, capable of being stretched like rubber. Crystal growth soon sets in, accompanied by molecular aggregation, and the mass reverts to ordinary brittle sulfur.

A. Smekal (Zeit. Physik., 1929, 55, 289) has pointed out that the properties of solids should be put into two general groups:

(1) *Structure-Insensitive Properties*, which show the same order of magnitude both with single crystals and with polycrystalline aggregates, *e.g.*, density, energy content, thermal coefficient of expansion, X-ray lattice structure, etc.

(2) *Structure-Sensitive Properties*, which vary materially on plastic deformation, changing grain-size, or the presence of impurities, *e.g.*, elastic limit, breaking strength, thermal and electrical conductivity, etc.

In pursuing this line of thought, F. Zwicky (Proc. Nat. Acad. Sci., 1929, 15, 816) advanced the view that ideal crystals, though dynamically stable, are thermodynamically unstable. Zwicky says that the thermodynamically stable forms are completely characterized by the space lattice deducible from X-ray structure analysis, but that superimposed upon this primary structure is a secondary structure also of perfect regularity, generally indicated by a slight periodic variation in density. The spacing of the elements of this secondary structure he estimates, for most crystals, to be in the region between 10 and 1,000  $m\mu$ , which includes colloidal dimensions. The X-ray evidence indicates that crystal surfaces are full of extremely fine cracks which determine planes of fracture, just as the "scratch" of a glazier's diamond directs the line of fracture in glass. Zwicky attributes these cracks to the secondary structure.

It has been observed that when metal parts fail, the fracture has often started at a place where there was an imperfection, *e.g.*, the die mark of the maker's name. Good shop practice demands a smooth, well-polished surface, not only for appearance but for strength as well. The X-ray evidence also indicates that atomic or molecular orientation (see p. 99) within a crystal will account for differences in strength along various cleavage planes, "weak" planes corresponding to those directions between the "unit cells" where electronic bonds are weakest.

*Adhesion.* When a substance is placed between two surfaces to which it clings, it may function as an *adhesive*, or as a *lubricant*, according as the free ends of the molecules, away from the surfaces, form a strong or a weak bond together. Thus Dr. W. R. Whitney (General Electric Co.) likened the molecules of a lubricant to rats with their teeth firmly fixed in the lubricated surfaces, which slide past each other over a surface of waving tails.

The investigations of J. W. McBain and D. G. Hopkins (Second Report on Adhesives and Adhesive Action, Adhesives Research Committee, London, 1926) show that joints are of two kinds:

(1) *Mechanical joints*, where the film of adhesive becomes embedded in the pores and asperities of the surfaces joined (as an extreme case).

(2) *Specific joints*, possible only in highly polished surfaces, due to specific molecular attraction between the surfaces and the adhesive.

Where both factors cooperate, they strongly reinforce each other. Any fluid which wets a particular surface and is later converted into a tenacious mass by cooling, evaporation, oxidation, etc., must be regarded as an adhesive for that surface. J. W. McBain and W. B. Lee (Proc. Roy. Soc. Lond., 1926, *112A*, 62) cemented together metal plates with various chemical compounds, and found that many of them functioned as adhesives, though they varied in strength with the metals joined.

(1) *Strong adhesives* (1,000±lbs. per sq. in.).

Rochelle salt, glucose, triphenylcarbinol, benzil, salicin, cholesterol, *p*-hydroxybenzaldehyde, T.N.T. (2, 4, 6, trinitrotoluene).

(2) *Medium-strong* (700±lbs. per sq. in.).

Benzophenone, coumarin, thallium salicylaldehyde, biuret, saligenin (after heating to resinification), *p*, *p*-diaminodiphenylmethane.

(3) *Weak adhesives* (500 lbs. per sq. in., or less).

Phenanthrene, thallium maleate, camphene, sodium palmitate (m. p. 316° C.), salol (joint inoculated with a crystal to cause setting), saligenin (heated only to its melting point).

Pure liquids function as adhesives, providing sufficiently thin layers are obtained, *e.g.*, by "wringing" together optically plane metal discs. McBain and Lee found the following breaking loads (lbs. per sq. in.) :

Water.....	14.7 to 36	Linseed Oil.....	11.8 to 18.5
Oleic Acid.....	up to 10	Benzene.....	up to 10.2
Olive Oil.....	up to 12	Iodobenzene.....	6.5 up to 20
Triolein.....	7.2 to 10.1	Ethyl Phthalate.....	up to 21
Castor Oil.....	7.2 to 9.1		

In 1875 Tyndall "wring" together two carefully surfaced plates, and by suspending them *in vacuo* proved that their adherence was not entirely due to atmospheric pressure, as is the case with the so-called Magdeburg cups. Tyndall believed that partial "molecular contact" accounted for the adherence *in vacuo*, but Lee (Science Progress, 1930), after considering all the evidence, concludes that molecular attraction may extend outward

to hundreds of molecular diameters. A reasonable explanation for this would be a *chain effect in molecular orientation* which simulates a large direct range of attraction, as suggested by McBain and by Sir W. B. Hardy in 1927. This view is supported by the following experiment:

A rod is carefully ground to fit a hollow cylinder, and is then smeared with a trace of paraffin. On inserting the rod, it continues to slide in, unless it be allowed to remain quiet for a few moments. In this case, the paraffin film "freezes" or "goes solid," but may be "fluidified" by striking the rod with a heavy hammer, accompanied by a twisting of the rod. Organization or orientation of the paraffin molecules to form chains of "fibers" whose ends grip the opposing surfaces, seems a likely explanation.

A practical aspect of adhesion crops out when local overheating causes carbonaceous material to "burn" to the bottom of laboratory flasks or stills, or of kitchen pots. While slightly scorched material is easily removed, deeply browned material holds tighter and is best removed, after drying, by kerosene, or mild abrasives and soap. Highly carbonized, blackened material is "burned on," and even scratching with steel or hard abrasives will leave some adhering remains. The simpler compounds (including "free carbon") produced by the more profound decomposition, seem to have the most powerful "nascent" free fields of force. A similar phenomenon appears in automobile cylinders, where newly-formed "carbon" is a source of trouble. Since most of it is loosened by acetone while hot, it is evidently not pure carbon, but a mixture of polymerized material perhaps containing some carbon.

The following remarks of Thomas Graham are still opportune (Proc. Roy. Soc. Lond., June 16, 1864, pp. 335-6) :

"A dominating quality of colloids is the tendency of their particles to adhere, aggregate, and contract. This idio-attraction is obvious in the gradual thickening of the liquid silica sol, and when it advances leads to pectization. In the jelly [of silicic acid] itself, the specific attraction in question, or *synaeresis*, still proceeds, causing separation of water, with the division into a clot and serum; and ending in the production of a hard stony mass, of vitreous structure, which may be anhydrous, or nearly so, when the water is allowed to escape by evaporation. The intense *synaeresis* of isinglass dried in a glass dish over sulphuric acid *in vacuo*

enables the contracting gelatin to tear up the surface of the glass. Glass itself is a colloid, and the adhesion of colloid to colloid appears to be more powerful than that of colloid to crystalloid. The gelatin, when dried in the manner described upon plates of calc spar and mica, did not adhere to the crystalline surface, but detached itself on drying. Polished plates of glass must not be left in contact, as is well known, owing to the risk of permanent adhesion between their surfaces. The adhesion of broken masses of glacial phosphoric acid to each other is an old illustration of colloidal synaeresis.

"Bearing in mind that the colloidal phasis of matter is the result of a peculiar attraction and aggregation of molecules, properties never entirely absent from matter, but more greatly developed in some substances than in others, it is not surprising that colloidal characters spread on both sides into the liquid and solid conditions."

*Crystallization.* When the atoms or molecules of substances arrange themselves in an orderly space lattice, there emerges the orderly structure we call a crystal. As P. P. von Weimarn has pointed out, crystals *tend* to purify themselves; that is, as the crystal lattice forms out of the crystallizing substance, it forces out stranger molecules which usually remain in the mother-liquor. But the course of crystallization, like the course of true love, does not always run smooth. Stranger ions, atoms or molecules are often very powerfully adsorbed by the growing or finished crystal, despite the repeated crystallizations generally necessary to secure reasonably pure crystals. "Water of crystallization" is often held and adsorbed colloids may completely alter the appearance of the crystal forms (see p. 26). Even the reaction of the solvent may be important. Thus sodium chloride forms cubes when crystallized from slightly acid water, but octahedra from slightly alkaline water.

Where the final mass of crystals forms a coherent solid, it often happens that the impurities present have accumulated as an inter-crystalline matrix which affects the practical properties of the solid. Thus, as W. J. Humphreys points out (Science, 1934, 79, 562) in the case of natural waters, the intercrystalline matrix melts at a slightly lower temperature than the ice crystals, because of the salts, dirt, etc., there present. This melting results in honeycombed or "rotten" ice, which fragments when the whole

ice-sheet is sufficiently weakened to be broken up by a storm. The fragments then melt rather rapidly in the heavier warmer water (about  $39.4^{\circ}$  F.) churned up from the lower levels, a fact often erroneously believed to indicate that the ice has become heavy and has sunk.

Crystallization is not a criterion of absolute purity—in fact, certain salts regularly crystallize together. Furthermore, crystallization is no evidence that a substance may not also exist in the colloidal state, for as P. P. von Weimarn has shown (see Alexander's Colloid Chemistry, Vol. I), practically all substances may be made to assume either the colloidal or the crystalloidal form. Many substances termed "amorphous," "vitreous," and exhibiting a glassy, conchoidal, or botryoidal structure, have been shown by X-ray analysis to be cryptocrystalline or to consist of colloidal crystals (see p. 27). The criterion of colloidality is particle size, not orientation in a space lattice.

Many substances most commonly known in the colloidal state have been crystallized, *e.g.*, gelatin, albumin, rubber hydrocarbon, pepsin and trypsin. (See *e.g.*, J. H. Northrup and M. Kunitz, Science, 1931, 73, 262; 1933, 78, 558; W. H. Smith and C. P. Saylor, J. Research, Natl. Bureau of Standards, Oct. 1934, Research Paper RP 719, on rubber hydrocarbon).

Extreme care is necessary to grow large well-formed crystals, and the temperature must be controlled within very narrow limits. R. W. Moore (J. Am. Chem. Soc., 1919, 41, 1060) was able to grow clear, perfectly developed crystals of Rochelle salt 3 inches long, in a thermostat sensitive to about  $0.01^{\circ}$ . He found that the crystals grew faster near the bottom of the crystallizing vessel than near the top, which is evidence of a gravitational accumulation of molecular groups at the bottom, quite analogous to the concentration of particles in colloidal solutions, as demonstrated by J. Perrin. (See also, J. Alexander, Trans. Am. Inst. Mining and Met. Eng., 1920). This observation also has the further implication that *crystallization often, if not generally, occurs by the deposition or aggregation of colloidal groups*, rather than by the placement of discrete atoms, ions, or molecules in a space lattice.

This view is borne out by the following simple experiment: To a solution of sulphur in carbon bisulphide there is added some Canada balsam, which serves to slow down and interfere with



the crystallization of the sulphur. A small drop of this solution is placed on a microscopic slide, rubbed out to a thin layer, and blown upon so that the solvent evaporates quickly. On examining the slide microscopically, especially with dark-field or ultramicroscopic illumination, the following will be found: (1) areas covered with tiny spherulites, in random but even dispersion; (2) long, branching, or grouped dendrites; (3) sulphur crystals, many of which show adhering ultramicros, which were unable to find closer lodgment in the crystal lattice. The areas about both the crystals and the dendrites were stripped free of spherulites, showing that these latter had been seized upon as the sulphur strove toward crystallization. Some groups of spherulites gave the appearance of incipient crystallization, for they had a semblance of order, and vacant spaces were beginning to appear among them. (See J. Alexander, First Colloid Symposium Monograph, Univ. of Wisconsin, 1923.)

The usual course of crystallization seems, therefore, to proceed according to the following steps: (1) As drop in temperature or loss of solvent lead to diminution in the capacity of the solvent mass to hold the solute in true solution, ions, atoms, or molecules of the solute are extruded, and aggregate according to the laws of chance, forming crystalline or truly amorphous groups ("*crystallogens*"), according to the substance and the conditions; (2) When the "*crystallogens*" become large enough to have a sufficiently reduced kinetic activity, they are aggregated into spherulites by interfacial tension against the "mother liquor"; (3) The spherulites aggregate into groups or into dendrites; (4) The groups or dendritic chains of spherulites slip or re-orient into a crystal, which may be large or small according to conditions.

Dr. Wm. M. Ord ("*The Influence of Colloids upon Crystalline Form and Cohesion*," London, 1879, Chapter II), who was activated by George Rainey, a pupil of Graham, discussed "the processes by which the modification of the crystalloid to the spheroidal form is effected," as per the following resumé:

(1) A new salt, formed by decomposition, is caused to combine in its nascent state with a colloid, which "may be of the proteid or gelatinous kind, or amyloid, or pectous, or an isomeric modification of an organic crystalloid, as uric acid, or of an inorganic crystalloid, as silica or silicates, peroxide of iron, etc.

Thus Mr. Rainey mixes two gummy solutions \* of the reacting salts; Prof. Harting (Univ. of Utrecht) places the solid salts at different points of an albuminous solution; in my own plugged tubes the reacting solutions are placed on opposite sides of a thick colloid dialyzer, within which they meet and undergo mutual decomposition. A modification of this condition is employed when urate of soda is formed by boiling uric acid with strong solutions of chloride of sodium or phosphate of sodium. The urate comes down in a colloidal state, and affects included crystals as any other colloid would."

"(2) A crystalloid is deposited from solution in the presence of a colloid. This occurs . . . in uric acid and urates mixed with albumen and mucus, in nitrate of urea crystallized from albuminous urine."

"(3) Crystals are broken down and turned into spheroids or molecules,† by the action of colloids into which they are introduced—a condition constantly seen in microscopical preparations. Crystals of uric acid, carbonate or oxalate of lime, etc., when preserved in gelatin or glycerine or glycerine-jelly, speedily lose their transparency, lose their sharp outline, and progress in various degrees towards sphericity. (Quart. J. of Microscopic Science, 1873.) The transformation of crystals of murexide put up in glycerine is a particularly beautiful phenomenon, exquisite needles growing at the expense of brilliant purple prisms." ‡

Prof. Harting had laid great stress upon the fact that in the first group just above mentioned, the crystalline material is in a "nascent state" and Dr. Ord, commenting on this, said: "The probability suggests itself to me that the nascent state is allied to or even identical with the colloid state of matters. Just as chemical substances may be either gaseous, fluid, or solid, as some are commonly seen in all states, some only in one, while many which we are accustomed to see only in one may by special experiments be brought into the other forms, so it seems to me probable that all matters, when deposited from solution, or other-

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\* This is a case of double colloidal protection (see p. 155). We also see how clearly those under Graham's influence understood that the same substance could exist as either crystalloid or colloid.

† Here used in the sense of small particles. (J. A.)

‡ A discussion of dropwise or *guttulate separation*, especially as applied to medical matters, is given by Prof. H. Schade (Univ. of Kiel) in Vol. II of Alexander's "Colloid Chemistry."

wise assuming a solid form, a liquid or gaseous form, have, or tend to have, a colloid and a crystalloid stage, both of which may be well marked, as in silica, or one of which may be more marked than the other, as in uric acid, or only one of which may be at present recognized, as in chloride of zinc on one side, in albumen on the other. . . . How far, again, is the energy of nascent bodies due to some sort of colloid state, allowing of more ready interpenetration of their molecules by combining substances—to something like a spongy state, offering enormous and facile contact?"

*Mesomorphic States.* Between the two extremes represented by the purely random, haphazard assemblage of molecules found in the truly amorphous state, and orderly arrangement in a space lattice, we find in certain substances a number of *partially* ordered arrangements termed by Prof. G. Friedel (University of Strasbourg) "*mesomorphic states*" (see his paper in Alexander's "Colloid Chemistry," Vol. I, with references to O. Lehmann's "liquid crystals").

Where molecules are all held in one plane and yet are scattered at random in that plane, somewhat like skaters on ice, we have the *smectic* or soap-like state. Where molecules are held in a line, and yet are free to swing at random about that line, like keys strung on a rod or wire, we have the *nematic* or worm-like state.

*Cholesterin caprate* is one of the few substances to exhibit both the smectic and the nematic states, and therefore shows three "melting points," as follows:

Cold, it is a crystalline solid

55°.5 C., smectic state; becomes pasty	} reversible, discontinuous transformations; product anisotropic and birefringent
68°.5 C., nematic state; remains pasty	
85°. C., it becomes a truly amorphous liquid	

Most substances in the nematic state are fluid. Among those showing this state are *p*-azoxyphenetol between 135° and 165°, and *p*-azoxyanisol between 116° and 133°. Among the substances showing the smectic state (besides soap) are ethyl-*p*-

azoxybenzoate between  $114^{\circ}$  and  $120^{\circ}$ , and ethyl-*p*-azoxycinnamate between  $140^{\circ}$  and  $250^{\circ}$ . The 10-bromophenanthrene-6-sulphonic acid of Sandquist is anhydrous and crystalline at ordinary temperatures. On the gradual addition of water without changing the temperature, it suddenly goes over into the smectic state, and with more water, into the nematic state, and finally into the amorphous state of true solution.

These partially oriented states are probably of importance in some technical and biological processes, and the possibility of their existence must be kept in mind. Friedel thinks that the expression "melting point" should be abandoned as deceptive, and speaking of the mesomorphic state in colloids says: "A gold sol is a dispersion of crystalline units in a predominating amorphous liquid which imposes on the ensemble its amorphous structure; the other extreme, a zeolite, is a dispersion of amorphous elements (water) in a predominant crystalline substance which imposes on the mass its crystalline structure."

*Molecular Orientation.* Most of the surface properties of matter are determined by the precise nature and orientation of the rind or external molecular layer, and are, like beauty, only skin deep—or even less than that, for as Langmuir has shown (*loc. cit.* p. 86) the free fields of force emanating from a surface exercise a much greater effect on the *near* side of an adsorbed molecule than they do on its *off* side.

The chemical behavior of atoms depends on the nature of their outermost electron rings. Similarly, the behavior of molecules is governed by the specific residual electronic fields they expose, and these depend on how they are oriented, that is, placed in or at an interface. A simple experiment of Devaux shows this (see Smithsonian Annual Reports, 1913). He floated a lens-shaped drop of molten fatty acid on the surface of some hot water, and allowed it to cool and solidify there, so that the upper surface of the lens cooled in contact with air, while the lower surface cooled in contact with water. After careful drying, the lower surface could be wet by water, but the upper surface could not. Apparently the hydrophile or friendly-to-water ends of the fatty acid molecules were turned outward in the surface that had cooled in contact with the water, while the hydrophobe or "greasy" ends were turned outward in the surface which had

cooled in contact with the air.\* It would seem that the direction in which the molecules of fatty acid turn or orient themselves at the surfaces depends upon which of their "ends" shows a greater attraction for the molecules of the exterior medium (air and water) than for the mass of fatty acid molecules on the interior of the drop. Since these attractions are the result of residual electronic fields, the phenomenon may be called *electroversion*. It shows how the nature of a medium may effect the behavior of particles dispersed in it.

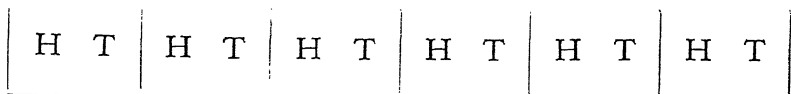
Langmuir says that molecules usually orient themselves in definite ways in the surface layer, since they are held there by forces acting between the surface and particular atoms or atomic groups in the adsorbed molecule. This accounts for the influence of chemical composition on adsorption commented on by Bechhold and others. Harkins (J. Am. Chem. Soc. 1920, 42, 706) points out that in organic compounds this orientation depends upon the dissymmetry of the molecule. "An entirely symmetrical molecule (or atom in the case of monatomic liquids) would not orient at all, but such a molecule or atom does not exist. Molecules as symmetrical as those of the short chain saturated paraffins, carbon tetrachloride, etc., would not be expected to show such evidence of orientation as those molecules which may be considered as heavily loaded, from the standpoint of the stray electro-magnetic field, at one end of the molecule and very light, in the same sense, at the other."

Katharine B. Blodgett, working in Langmuir's laboratory (General Electric Co.) deposited monomolecular layers of calcium and other metallic soaps on various surfaces—glass, chromium, nickel, brass, steel, cast iron, silver and platinum. The films could be of one substance, or composite, and they could exceed 200 layers (J. Am. Chem. Soc., 1935, 57, 1007-22). By appropriate experimental procedure (for which the original paper must be consulted), the successive layers could be oriented all *one way*, or else *alternately*, as indicated in the diagram below, where H represents the metallic "head" of a molecule, *e.g.*,

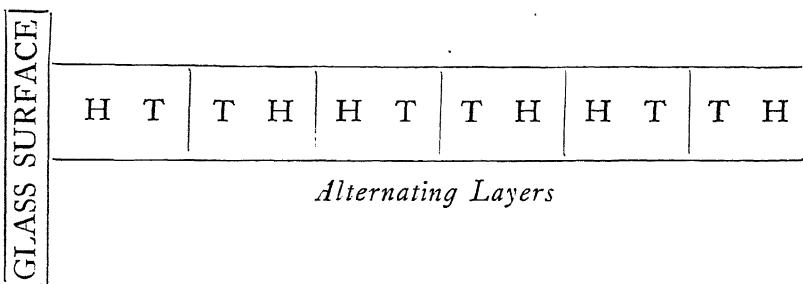
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\* The view has been expressed that the wettable surface binds a film of moisture which enforces the outward orientation of the hydrophile ends of the molecules.

( $-\text{COOH}$ )<sub>2</sub>Ca, and T represents the hydrocarbon "tail" of the molecule.



*Non-alternating Layers \**



*Alternating Layers*

A certain *time* is needed for a film to attach itself to glass, and this is governed by the temperature, pH, and metallic salt content of the water on which the soap films are formed. "A film in which all the molecules are oriented with the  $\text{CH}_3$  groups at the upper surface possesses the exceptional property that neither water nor oil will wet the surface."

Langmuir and Schaefer (J.A.C.S., 1936, 58, 284) skimmed off and analyzed the monomolecular films of stearic acid formed on water containing calcium or barium salts (concentration  $10^{-4}$  molar with respect to carbonate). When the water was strongly alkaline (pH 11) the films are nearly pure neutral soaps, but consist of free fatty acid when the pH of the water is 3. "Half-conversion to neutral soap occurs at pH 5.1 for calcium and pH 6.6 for barium solutions. These metallic constituents of the films have a profound effect upon the physical properties. They increase the rigidity of the films and affect the ease with which multimolecular films can be formed on metal or glass."

*Dipoles and Dipole Moment.* From recognition of the fact that molecules have various and variable shapes and space dis-

\* These cannot be deposited next to glass, indicating a warping of the electronic fields of the molecular layer next to the glass.

tributions, arises the concept of electrically symmetrical or *non-polar* molecules, *e.g.*,  $\text{CCl}_4$ ,  $\text{CH}_4$ , and unsymmetrical or *polar* molecules, *e.g.*,  $\text{CHI}_3$ ,  $\text{CH}_3\text{CH}_2\text{COOH}$ . The unbalanced molecules, or *dipoles*, are lopsided and have what is termed a *dipole moment*. A matter of consequence is spoken of as a matter of great moment, meaning great potency or importance. The dipole moment (or potency) is measured by the *amount* of the electrical unbalance, multiplied by the *length* or leverage over which it acts.

As Debye and Hückel have pointed out, if non-polar molecules approach close enough, their electric fields may mutually distort each other, so that an electrical unbalance or polarity will develop and a dipole moment come into evidence. Consequently, when molecules are forced together, as under increased pressure, adsorption at surfaces or within capillary pores, reactions may be facilitated or initiated (see p. 83 and p. 86). Increase in temperature, within certain limits, "swells" or "opens out" molecules and atoms, increasing the probability of their passing from one low potential position through or past a high potential position, to another low—that is, of undergoing a chemical readjustment.

Some understanding of the size, spatial arrangement, shape and electronic fields of many organic molecules in crystals is given by the X-ray spectrographic investigations now being conducted, especially in the Faraday Research Laboratory of the Royal Institution, under Sir William Bragg (Nobel Laureate). In Figures 4-9 are reproduced some of the results for dibenzyl, naphthalene and durene, obtained by Dr. J. Monteith Robertson (Proc. Roy. Soc. Lond., 1933, *142A*, 674-88; 1934, *146A*, 474-82; Nature, 1934, *134*, 381; Proc. Roy. Soc., 1935, *150A*, 348-62; *ibid.*, 1933, *142*, 666 *et seq.*) See also Sir William H. Bragg (Nobel Laureate), J. Inst. Elect. Engrs., Kelvin Lecture, Dec., 1935. Thanks are due to the authors for their cooperation in reproducing these illustrations.

## EMULSIONS AND EMULSIFICATION

An emulsion is a very fine dispersion of one liquid in another with which it is immiscible. The stability or "life" of the emulsion will depend upon a variety of factors, chief of which is the presence or formation of a third substance or phase which can serve as a stabilizing or emulsifying agent.

If water and benzol are agitated together, on standing the dispersed benzol droplets quickly unite and the liquids separate into two layers, because their interfacial tension is very high (about 35 dynes per sq. cm.). Where the percentage of benzol is small and the agitation violent enough to reduce it to tiny droplets, the separation process will take quite a time, so that the dilute fine emulsion will have a limited "life". However, if the aqueous phase consists of sodium oleate (Castile soap) solution

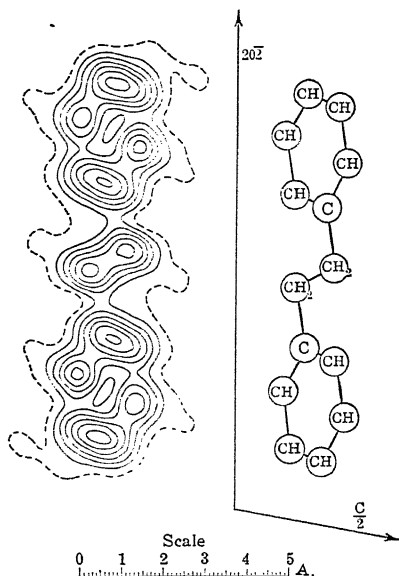


FIG. 4. Projection of dibenzyl molecule along the  $b$  axis. Each contour line represents one electron per  $\text{\AA}^2$ .

0.01 normal or stronger, the interfacial tension will be reduced to about two dynes per sq. cm. and vigorous agitation will give a stable emulsion. As J. Willard Gibbs demonstrated thermodynamically, the sodium oleate, tending to reduce the interfacial tension, accumulates at the interface, and practically surrounds the emulsified droplets with a coherent, stabilizing film.

The pioneer work of Ascherson has been mentioned on p. 2, and was also discussed at some length by Dr. Wm. Ord in his book "The Influence of Colloids on Crystalline Form and Cohesion" (London, 1879). More recently, W. Ramsden (Proc.



Roy. Soc., 1903, 72, 156-61) studied surface membranes, bubbles emulsions and mechanical coagulation, and showed that in many cases the stabilizing substance could be so concentrated at the "*dimeric interface*" (the interface between two liquids) that it would be precipitated as a solid or semi-solid film. This form of separation is actually used in "shaking out" the colloidal albumins in beer with benzol, so as to estimate the amount present. It is markedly shown in saponin (soap-bark) foam, for the air can be sucked out of its bubbles and the saponin film will fold up like a collapsed balloon. (Ramsden effect.)

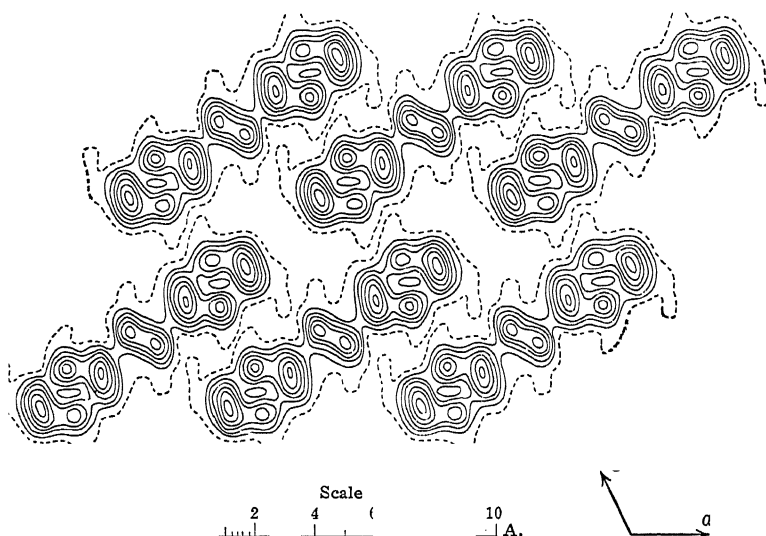


FIG. 5. Projection of dibenzyl molecules along the  $b$  axis showing the relations of a group of molecules in the crystal.

Prof. F. G. Donnan (University of London), with a pipette which permitted drops of oil to rise through water and various alkali solutions, found that while colza oil had a "drop number" of 88 in pure water, in  $N/1000$  NaOH the drop number rose to 306, and with slightly stronger alkali the oil streamed into so fine a dispersion that the number of drops could not be counted. Donnan later showed that if the oil was freed of all traces of fatty acid (which appears in rancidity and forms soap with the alkali) the drop number in water and in alkali was the same; and further,

by experiments with emulsion of hydrocarbon oils containing various fatty acids, he found that the dispersive effect was shown markedly only by lauric acid ( $C_{12}$ ) and those higher in the series. He concluded that the adsorbed viscous or gelatinous layer of soap about the globules prevented their coalescence, thus stabilizing the emulsion.

Given two immiscible liquids, it is obvious that either one might be the dispersed phase. Thus, considering oil and water, we may have an emulsion of oil-in-water (O/W), or an emulsion

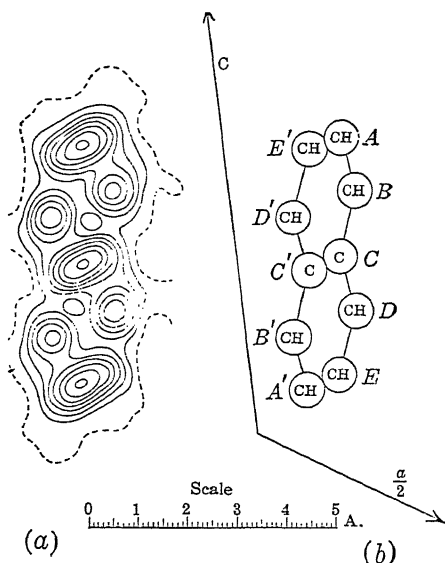


FIG. 6. Projection of naphthalene molecule along  $b$  axis. Each contour line represents one electron per  $\text{\AA}^2$ .

of water-in-oil (W/O). Cases are known where droplets of water containing within them dispersed particles of oil, are dispersed in a homogeneous oil phase, thus constituting a *duplex emulsion*.

What factors determine whether there will be formed an oil-in-water or a water-in-oil emulsion? Where the emulsifying agent is a soap, the generally accepted view of molecular orientation or oriented adsorption at the interface between the two liquids leads us to the idea that the hydrocarbon end of soap will

direct itself toward the oily liquid, while the metallic end will point toward the aqueous phase. If, now, the fatty ends of the molecule can pack together closer than do the metallic ends, the interfacial film bends *toward the oil*, and we have an emulsion of oil in water. This is the case with sodium, potassium and caesium soaps; and indeed Finkle, Draper and Hildebrand found that the size of the oil drops in emulsions, made with soaps of these alkali metals, varied as this theory demands [J. Am. Chem. Soc., 45, 2780 (1923)].



FIG. 7. Projection of naphthalene molecules along  $b$  axis showing mutual relation of molecules. Each line represents one electron per  $\text{\AA}^2$ .

If, however, a soap of a bi- or trivalent metal (calcium, aluminium, magnesium, lead or the like) be used, which has several hydrocarbon chains attached, then the interfacial film bends *towards the water*, and we have an emulsion of water in oil. Thus are explained the observations of G. H. A. Clowes on the reversal or inversion of emulsions and the variation in the number of drops when oil is dripped into various solutions from a stalagmometer (drop measurer).

W. D. Harkins and his collaborators have developed the principles governing this oriented wedge theory of emulsions and the inversion of emulsions [see J. Am. Chem. Soc. 39, 587 and 592-4 (1917); also "Science," May 23, 1924].

Few emulsions follow this simple theory. The stabilizing layers are often many molecular layers deep and are affected in their structure by impurities (salts, etc.). In 1910 S. U. Pickering (Kolloid Zeit., 7, 11) called attention to the fact that very stable emulsions of the oil-in-water type could be stabilized by fine powders of substances insoluble in either liquid. Prof. W. D. Bancroft (Cornell University) came to the following conclusion (J. Phys. Chem., 1927, 31, 1681): "At present there is no absolute method of predicting the type of emulsion from any other property than the surface tensions of the film. In most cases it

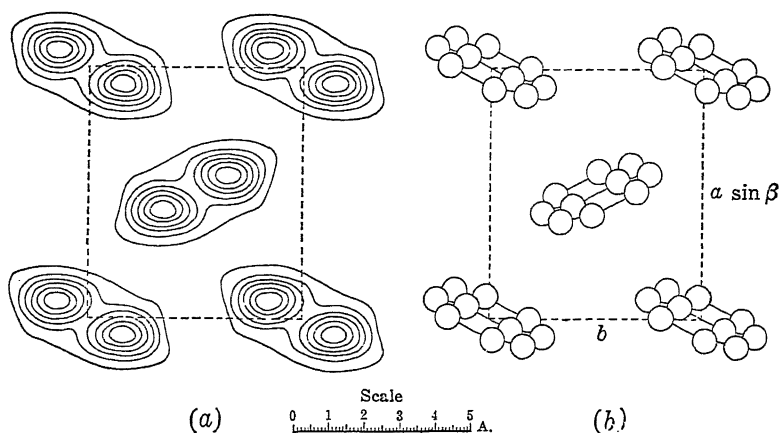


FIG. 8. Projection of naphthalene along *c* axis. Each contour line represents two electrons per Å<sup>2</sup>.

is satisfactory to say that the liquid which wets or peptises the emulsifying agent the more readily is the dispersion medium; but this generalization in this form breaks down for benzene, oleic acid and water; for benzene, iodine and water; and, doubtless, for many other cases."

Anyone who has tried to make emulsions, *e.g.*, mayonnaise, will realize that the order, speed, and amount of mixing are factors of great importance.

Dr. Wm. Clayton (Chemistry and Industry, 1932, 51, 129-39) states: "The ultimate stability of an emulsion depends on several factors. Enhancing stability will be: (1) fine dispersion of the globules; (2) a minimum difference in the densities of the

two phases; (3) a viscous continuous phase; and (4) a stable film around the globules. For the last factor, time may be necessary to permit adequate adsorption of the emulsifying agent, accompanied in some cases by de-solution due to denaturation. We are led immediately to the conclusion that a given emulsifying agent plays two parts: (1) it permits easy dispersion owing to reduced interfacial tension, and (2) it may promote stability after

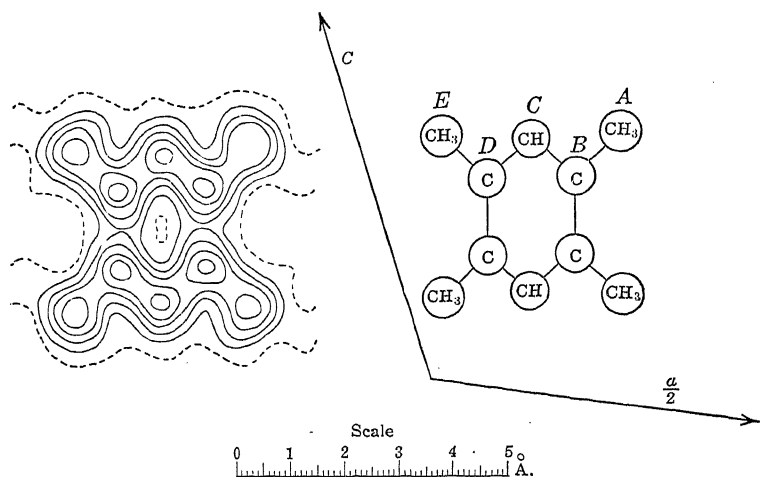


FIG. 9. On the left is the electron map of a molecule of durene. The electron density is projected upon the  $ac$  plane of the cell which contains the unit of pattern. The contour lines are graded by steps of 1 electron per Angstrom unit of area, i.e., per  $10^{-16}$  cm<sup>2</sup>. The accuracy in the denser parts of the figure is about that represented by the width of a contour line. On the right is the diagrammatic arrangement deduced from the electron map.  $a = 11.57$ ;  $b = 5.77$ ;  $c = 7.03$ ; is perpendicular to  $ac$ ; the angle between  $a$  and  $c$  is  $113.3^\circ$ . [J. M. ROBERTSON, *Proceedings of the Royal Society, A*, 1933, vol. 142, p. 666.]

its adsorption, assuming the absence of disturbing factors such as chemical change or such physico-chemical alteration as leads to syneresis. Choosing conditions, one can both make and 'break' emulsions by agitation."

Prof. T. R. Briggs (Cornell University) found intermittent shaking very much more effective than continuous shaking in making emulsions—"six hundred or even a thousand times more effective" . . . (J. Phys. Chem., 1920, 24, 120). The United States Dispensatory (19th ed., p. 444) states: "Some skill and care are required for the production of uniform and perfect

emulsions"; and it describes the usual method employed here (U. S. A.) and that used abroad. In the former, oil is added to twice its amount of gum arabic mucilage (for example) with thorough mixing, and gum solution and oil are added alternately, never allowing the oil to be in excess. The "Continental" method is to mix oil with the dry gum, and then to add enough water to make a thick "nucleus" which can be diluted further. The proportions recommended are one part of gum to two or three of oil,

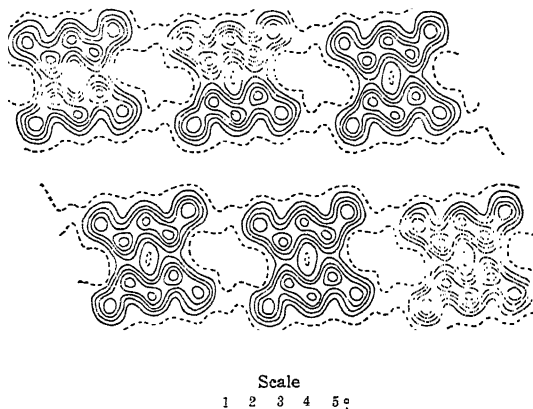


FIG. 10. A series of durene molecules projected on the *ac* plane. This shows the relative spacings of the molecules in the crystal. [J. M. ROBERTSON, *Proceedings of the Royal Society, A*, 1933, vol. 142, p. 667.]

with two parts of water to make the nucleus. Further remarks about emulsions will be found elsewhere (pp. 212).

## 2. ELECTRIC EFFECTS

In general, when two substances are brought into contact, the one having the *higher* dielectric constant becomes *positively* charged, whereas the one with the *lower* dielectric constant becomes *negatively charged* (A. Coehn, *Wied. Ann. Physik.* 1898, 64, 217). Since water has a high dielectric constant (80), most substances suspended in pure water become negatively charged and wander to the anode. On the other hand, if suspended in oil of turpentine, which has a low dielectric constant (2.23), they become positively charged and wander to the cathode.

If, however, electrolytes are present, as they usually are, Coehn's law is superseded by other controlling factors, such as the adsorption of ions, which may give their charge to the suspended particles. In fact Hardy found that in pure water albumin was amphoteric; in the presence of a trace of alkali it acquired a negative charge and migrated to the anode; but a

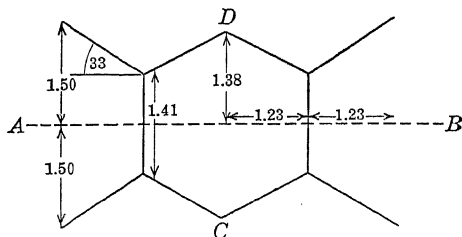


FIG. 11. Dimensions of the Durene Molecule, in Å.

trace of acid gave it a positive charge and it then migrated to the cathode. The following table shows the usual charge and migration tendency of a number of *aqueous* colloidal solutions.

Charged + Migrate to Cathode (— Pole)	Charged — Migrate to Anode (+ Pole)
<ol style="list-style-type: none"> <li>1. Hydrates of Fe, Cu, Cd, Al, Zr, Ce, Th.</li> <li>2. Titanic acid.</li> <li>3. Colloidal Bi, Pb, Fe and Cu (Bredig's method).</li> <li>4. Albumin, hemoglobin, agar.</li> <li>5. <i>Basic Dyes</i>: Methyl violet, Bismarck brown, methylene blue, Hofmann violet.</li> </ol>	<ol style="list-style-type: none"> <li>1. Sulphids of As, Sb, Cu, Pb, Cd. Halides of Ag.</li> <li>2. Stannic acid, silicic acid.</li> <li>3. Colloidal Pt, Au, Ag and Hg, I, S, Se.</li> <li>4. Gum arabic, soluble starch, gamboge, mastic, oil emulsion.</li> <li>5. <i>Acid Dyes</i>: Eosin, fuchsin, anilin blue, indigo, soluble Prussian blue.</li> </ol>

### ELECTRIC CHARGE PATTERNS

The situation as to electric charges on particles is illustrated by the story of a Sunday school superintendent who, in examining a class, asked: "Now if every good little girl here were snow-white, and every bad little girl were coal-black—what color would *you* be?" And he pointed from one to another. Conscience-stricken ones admitted blackness, while the self-righteous claimed whiteness. Then up spoke truthful little Elsie: "Please, Sir, I think I'd be black and white, speckled all over."

Material particles have their individual patterns of positive and negative areas, whose configurations vary with temperature and other conditions, according to changes produced in the arrangement of their constituent particles, molecules, atoms, and subatomic units. In many cases, however, the charges may be so balanced that a particle may *appear* neutral or without charge—especially if nothing gets close enough to it to be affected by the electronic “spottiness” responsible for the specificities in the reaction between particles when they come to close grips.

### HELMHOLTZ AND GOÛY LAYERS

The residual *outwardly* directed fields of a dispersed particle tend to surround it with a layer of particles having *inwardly* directed areas of opposite charge or specificity, forming what Helmholtz (H. von Helmholtz, Wied. Ann. Phys., 1879, 7, 337) called an *electric double layer*. In 1910, however, G. Goüy (J. physique 1910, (4), 9) pointed out that the electric influence of a particle must extend noticeably beyond the monomolecular layer adsorbed on it. This means that the transition between the fluid and a particle dispersed in it is not abrupt, but that the particle is surrounded by a diffuse aura or “atmosphere” of particles, molecules, or ions, whose concentration diminishes with distance from the attracting particle, just as the earth’s atmosphere becomes rarer the higher we ascend. However, the first layer is held by much stronger forces than the outer layers, and the influence of the surface is apparently transmitted through and modified by this first layer of molecules or ions, whose outwardly *exposed* fields are warped by the fixation.

### EPSILON AND ZETA POTENTIALS

These considerations indicate that the *total potential difference* (electric charge gradient) *transversely through* the depth of the Goüy layer (designated by the Greek letter epsilon,  $\epsilon$ , and called the *transverse potential difference*), must be greater than the potential difference existing *between two layers* of this same ionic atmosphere at some distance from the particle surface. Electronic forces affecting whole molecules diminish with distance much more rapidly than does gravitation—inversely as about the fifth power instead of inversely as the square. The forces affecting the near



and the far side of the first contact layer of molecules are of a higher order, and vary about as the inverse ninth power, so that even the trivial difference of molecular diameter makes a great difference in their strength. The actual surface film may be monomolecular and may cling so tightly to the surface as to move with it or slide along it.

The potential difference between two layers of the Goüy "atmosphere," is designated by the Greek letter *zeta*,  $\varsigma$ , and is termed the *tangential potential difference*. The following analogy will help one to see why this *zeta potential* ( $\varsigma$ ) will be less than the *epsilon potential* ( $\epsilon$ ): The total air resistance to a meteor plunging vertically through the earth's atmosphere will be greater than what it would encounter if it were to skim tangentially through the rare upper ranges of the atmosphere.

The transverse potential ( $\epsilon$ ) comes into play when particles *approach* each other *preliminary* to the formation of stable aggregates (as in coagulation or precipitation). The zeta potential then becomes effective and must be *below a certain critical value*, or else the particles repel each other so powerfully that the surface specificities are unable to become effective and "seat" the particles to each other into a stable group. This *first critical potential* is not quite the same for all electrolytes. It seems that the surface specificities or electronic areas of the molecules themselves here enter as a factor, and the coagulation takes time (*zone of slow coagulation*). Where the zeta potential falls to zero, practically every contact between particles results in lasting aggregation; that is, at this *second critical potential* there appears a *zone of rapid coagulation*. Between the first and the second critical potential lies the zone of slow coagulation which is the one that obtains in most biological and technical procedures. It may be followed visually in the ultramicroscope; the mutual repulsions of particles on unsuccessful approaches and their mutual fixation on successful approaches may be followed over many minutes or even hours by choosing suitable dilutions. In chemical analysis, where the relative unimportance of cost permits of high electrolyte concentrations, these may be used to speed coagulation.

For quantitative consideration of the many factors influencing precipitation and coagulation (*e.g.*, concentrations, temperature, mixtures of electrolytes, etc.), the reader must consult such books as "Colloid and Capillary Chemistry," by Prof. H. Freundlich

(London University) or one of the other treatises mentioned in the final bibliography. A few of the experimental data are here given by way of illustration.

Zsigmondy (Nachr. Ges. Wissenschaft, Göttingen, 1917, p. 1) added progressively larger amounts of NaCl (under fixed conditions) to a certain amount of a colloidal gold solution, and noted the time required for the mixture to coagulate. The coagulation is readily followed by the color change from red to purple. The results may be epitomized thus:

TABLE XI

Concentration of Coagulator, NaCl, in millimols per liter	Coagulation Time, in seconds
5	150
10	12
20	7.2
50	7.
75	6.5
100	7.
200	6-7.
500	7.

In Zsigmondy's "gold number" test (see p. 152) the precise amount of NaCl solution was chosen to cause the reaction to take place over a conveniently observable time interval.

Buxton and Teague (Zeit. physik. Chem., 1904, 57, 72, 79) coagulated a platinum sol by addition of  $\text{FeCl}_3$  in progressively increasing amounts. Their results may be condensed as follows:

TABLE XII

Concentration of Coagulator, $\text{FeCl}_3$ , in millimols per liter	Flocculation	Cataphoretic Migration
0.0208—0.0557	None	To <i>anode</i>
0.0833—0.2222	Complete	Does not migrate
0.3333—6.667	None	To <i>cathode</i>
16.33 —666.7	Complete	

In this case, it is evident that beyond a certain amount, the coagulator, or rather some of its ions, may be adsorbed and stabilize a sol, the charge of the colloidal particles being reversed. Friedmann and Niesser (Münch. Med. Wochenschr. (1903, 51, No. 11) and H. Bechhold (University of Frankfurt), Zeit.

physik. Chem., 1904, 48, 385) who first observed the phenomenon, termed it the *irregular series*. *Sensitization*, e.g., by minute traces of protective colloids (see p. 154) is evidently a related phenomenon.

### ELECTRO-KINETIC EFFECTS

The tangential potential difference ( $\zeta$ ) is what comes into evidence in the phenomena termed Endosmosis, Cataphoresis, Streaming Potential, and Migration Potential. These apparently formidable words express relatively simple experimental facts. Dr. Harold A. Abramson in A.C.S. Monograph No. 66 on "Electrokinetic Phenomena and their Application to Biology and Medicine," (Chemical Cat. Co., 1934, p. 331), gives an extensive study of these effects, and in Appendix III gives a list of patents covering their application to such problems as drying peat, electrodeposition of rubber latex, purification of clays, water, sugar, serum, glycerin and gelatin, separation of water/oil emulsions, impregnation, and tanning.

*Endosmosis* (Electro-endosmosis). In 1809 F. Reuss (Mém. Soc. Imp. des Naturalistes de Moscow, 2, 237) reported that if two tubes are filled with water are thrust into moist clay and an electric current is passed through the system from electrodes immersed, respectively, in the water of each tube, then the water will *rise* in the tube containing the *cathode*, and *fall* in the tube with the *anode*. This indicates a motion of water in the direction of the current, which is a stream of negative electrons, *entering* at the *anode* and *leaving* at the *cathode*. Positively charged ions (termed *cations*, e.g.,  $H^+$ ,  $Na^+$ ) follow the current towards the cathode (the *negative voltaic pole*), while negatively charged ions or *anions* (e.g.,  $O^-$ ,  $Cl^-$ ) move oppositely to the electron stream, towards the anode (the *positive voltaic pole*).

Later on Quincke (Ann. de Phys. u. Chem. 1861, 113, 513) showed that in some cases water could move oppositely to the direction first found by Reuss. We now believe that in these cases the water molecules or their ions are oppositely oriented at surfaces from what they were in the experiment made by Reuss.

*Cataphoresis* (also called *Electro-cataphoresis* or *Electrophoresis*). Even Reuss himself observed that fine clay particles which had become suspended in the water of his tubes after hav-

ing become loosened from the clay mass in his experiment (above referred to), moved through the water in a direction *opposite* to that in which the water was forced through the clay by the electric current. That is, they moved toward the anode (+ voltaic pole), which indicates that they had a negative charge, as is the case with most substances suspended in water (see Coehn's "Law" above), apparently because they orient the water molecules with their  $\text{OH}^-$  groups outward. With positively charged sols (*e.g.*, alumina) the reverse is the case.

*Streaming Potential.* If a liquid is forced through a porous membrane or a single capillary, a potential difference is set up between the opposite sides of the membrane or the opposite ends of the capillary, as was first shown by Quincke (Pogg. Ann. der Phys. 1859, 107, 1; 1860, 110, 38). Here the electric double layer is sheared by the pressure, the plus charges passing one way and the minus charges the other way.

*Migration Potential (also called Dorn Effect).* If particles, *e.g.*, of silver powder, are allowed to fall through a column of water, a potential difference is set up between the top and the bottom of the water column. This phenomena is like that of streaming potential, except that here the fluid is stationary and the particles and their surfaces move past it. (See Ann. der Physik, 1878, 5, 20; 1882, 9, 513; 10, 46.)

The relation between these phenomena is shown in the following table:

TABLE XIII

Phenomenon	Motivating Force	Fact Observed
Electro-endosmosis.....	Electromotive Force (Electric Current)	Liquid moves past solid surfaces
Cataphoresis.....	Electromotive Force (Electric Current)	Solid moves past liquid surfaces
Streaming Potential.....	Pressure, causing flow of liquid past surface	Potential difference is established
Migration Potential.....	Motion of surface past liquid	Potential difference is established

"Cascade electricity" is an illustration, commonly found in nature, of electrification by motion. A stream of water falling

through the air generally breaks up into drops, which then develop a charge or potential against the air. Solar radiation ionizes the atmosphere and showers it with electrons; but some part of the charge of clouds, leading to lightning flashes, is due to the motion of water droplets through the air.

Escaping steam may also build up high charges, the phenomenon having been first noticed by an engineer who was trying to stop up a steam leak. While holding one hand in the escaping steam, he touched the lever of the valve with the other hand, and received a violent shock. (See *Phil. Mag.* 1840, 17, pp. 370, 452.) Faraday, who investigated the phenomenon, found that it was not shown by *dry* steam, and attributed the development of the charge to friction between water droplets and whatever surfaces opposed their passage. Generally, the steam cloud developed a positive charge; but if some turpentine were added to the steam, the droplets became coated with a film of it, and the charge became negative. (For further details see any of the older books or articles on physics, the hydro-electric machine, etc., e.g., "Lectures on Electricity," by Henry M. Noad, London, 1844).

### 3. DIFFUSION EFFECTS

#### DIFFUSION AND DIFFERENTIAL DIFFUSION

The word "diffusion" is derived from the Latin *dis*, meaning *apart*, *asunder*, and the verb *fundere*, meaning *to pour out*. Diffusion is an auto-dispersion due to the kinetic activity of the particles (molecules, atoms, ions) of a substance which enables them to separate and to pass among the molecules of gases or liquids, or through the molecular framework of solids. If an ingot of pure gold be placed on one of pure lead, the two metals will slowly diffuse into each other, as Roberts-Austen found by making analyses of the two contact zones after the lapse of five years. With less dense solids and more active diffusing molecules the process is much quicker, as may be seen when an aniline ink diffuses out into the glycerin-gelatin of a hectograph.

Even with the kinetically very active gases, diffusion is relatively a slow process when compared with the effects of mechanical mixing, or of *convection*, which is a gross mixing of masses

of fluids due to thermal agitation. In making diffusion experiments with gases and liquids it is necessary to take extreme precautions to prevent the results being obscured by convection currents.

Diffusion may be responsible for motion. A bit of camphor fixed at the water level of the stern of a small "boat," will, by its superficial diffusion, drive the boat about, if the water surface be first cleaned by dusting on it some pure talcum powder (not the compounded cosmetic article) and then removing the talc layer with a clean metal scraper. Fine aluminum filings placed in dilute caustic soda evolve hydrogen slowly, and this causes the metal particles to move about, even though no visible gas bubbles appear. The motion of some diatoms and bacteria seems due to gas evolution, though many micro-organisms swim by the motion of their bodies or of cilia, tails, or similar appendages.

When activated units (ions, atoms, molecules) come within sufficient proximity, chemical reaction is practically instantaneous. The speed of reaction with large masses of matter, therefore, will depend primarily on how quickly the activated units can be brought together, despite the interference of the increasing amount of reaction product and the decreasing amount of reactants. Agitation and convection both facilitate reaction, but in their absence diffusion controls.

Where reactions take place at *interfaces*, i.e., the boundary surfaces between phases, the *diffusion* of reactants and the products of reaction into and from the surface, control reaction velocity. For example, iron can rust no faster than oxygen can get to the surface under attack. As W. G. Whitman points out (J. Soc. Chem. Ind., 1935, 54, 175T), in most cases of diffusion into interfaces there are two factors involved: (1) "*Eddy diffusion*," which is transfer up to the true surface film by turbulent mixing; and (2) "*Laminar diffusion*," representing movement through the true "stagnant" film.

Diffusion is also of importance in such physical phenomena as the condensation of mixed vapors, because the less volatile material must diffuse through a film of the more volatile in order to reach the chill condensing surface. In the open-hearth refining of iron, diffusion brings various impurities to the surface of the ingots of metal, just as it also brings oxygen to rusting iron, and hydrogen to metallic catalysts in the hydrogenation of oils. The

rotating electrodes, so much used in chemical analysis, reduce thickness of the surface film, thus speeding diffusion and permitting the use of higher current densities, so that the time of depositing the metal is shortened.

Many mixtures may be distilled without change in composition (*e.g.*, "95% alcohol," boiling at about 78° C.), and are known as "constant-boiling" or *azeotropic mixtures*. If such a mixture is vaporized by blowing a stream of air over its surface, that component which has the higher diffusive mobility will escape more readily, and the remaining liquid will change in composition. Thus, "95% alcohol" will leave a more dilute residue when air is blown over it or bubbled through it. To remove traces of water in chemical analysis, it is common to add alcohol to a mixture to "lift" the water out in a current of air or a stream of air bells or bubbles.

If diffusion occurs *into a jelly*, many interesting phenomena may develop, especially if the jelly adsorbs any of the diffusing substances or contains substances which can react with them.

Owing to the enormous surface they present, colloidal gels exhibit a powerful adsorptive action. In fact, even when percolated through such a relatively coarse-grained septum as sand, most solutions issue with a materially reduced content of solute, and benzopurpurin solutions may be thus decolorized. Further, if a solute hydrolyzes into ions having different degrees of adsorbability or different rates of diffusibility, they may be actually separated by diffusion through a colloidal gel.

This phenomenon is nicely exhibited by what may be termed a "patriotic test tube," prepared by filling a tube about two-thirds full with a slightly alkaline solution of agar containing a little potassium ferrocyanid and enough phenolphthalein to turn it pink. After the agar has set to a firm gel, a solution of ferric chlorid is carefully poured on top, and almost instantly the separation becomes evident. The iron forms with the ferrocyanid a slowly advancing band of blue, before which the more rapidly diffusing hydrochloric acid spreads a white band as it discharges the pink of the indicator. After the lapse of a few days the tube is about equally banded in red, white, and blue.

Even then the tubes do not cease to be of interest, for if they are allowed to stand several weeks the pink color is all discharged and there develop peculiar bands or striations of blue, apparently

due to the fact that the iron ferrocyanid temporarily blocks the diffusion passages, which are gradually opened again after a layer of the blue salt has diffused on from the lower surface. (*Liesegang's rings*.\*)

Not only may ions be thus separated, but if two solutes in the same solvent possess different rates of diffusion or different degrees of adsorbability, they also may be separated from each other by diffusion through a colloidal gel or septum. (*Differential Diffusion*.) See J. Alexander, "Selective Adsorption and Differential Diffusion," J.A.C.S., 1917.

### DIALYSIS AND ELECTRODIALYSIS

Colloid solutions possess a small but definite diffusibility through colloidal septa (parchment paper, bladder) as was recognized by Graham, who found that "tannic acid passes through parchment paper about 200 times slower than sodium chlorid; gum arabic 400 times slower."† Graham's original form of dialyzer may be made from a wide-mouthed bottle whose bottom has been removed.‡ The mouth is closed by a piece of bladder or parchment paper tightly bound on, the solution to be dialyzed is poured in, and the bottle immersed about halfway in water contained in a larger vessel. Most of the crystalloids diffuse through the membrane into the outer water, which should be frequently renewed, while most of the colloids remain in the original bottle, and may be thus obtained in a purified condition. Improved modern dialyzers consist of parchment or collodion sacs or thimbles, or even whole bladders, which have the advantage of a larger dialyzing surface.

The "star" dialyzer of Zsigmondy and Heyer (*Zeit. anorgan. Chem.*, 1910, 68, 169) consists of a shallow water-holding chamber with stellate ridges to support the dialyzing membrane, which

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\* Liesegang's rings, named after Dr. Raphael Ed. Liesegang, are of importance in mineralogy (agates), geology (ore deposits), and biology (rhythmic banded structures). See the extensive literature for various views as to the mechanism of their formation.

† It is commonly but erroneously stated, even in text books, that colloids do not diffuse or dialyze. The extent to which dialysis occurs depends mainly on the fineness of the colloidal particles, the nature of the septum, and *time*.

‡ A lamp chimney will answer very well, and a piece of kid glove will serve as a septum.



is supported by an ebonite ring. Cellophane,\* parchment paper and gold-beaters skin are among the membranes that can be used, but it is wise to test the perfection of the membrane before depending on the results.

By introduction of electrodes into the dialyzate and the exterior water, and the passage of a suitable electric current, the removal of diffusible material may be hastened. This process of *electro-dialysis* or *electro-osmosis* is employed commercially, as well as in the laboratory. This method was initiated by Morse and Pierce (Zeit. phys. Chem., 1903, 45, 589), who purified gelatin contained in a parchment membrane immersed in a stream of water, which washed away the diffusible electrolytes whose passage through the membrane was facilitated by an electric current.

### OSMOSIS AND OSMOTIC PRESSURE

Interference with the normal process of diffusion results in a condition of stress from which emerge the phenomena termed *osmosis* and *osmotic pressure*. Suppose that an aqueous solution of sugar is separated from pure water by a *semi-permeable* septum, that is a septum or wall which permits the passage of the solvent, water, but not the passage of the solute, sugar. At any instant, more water molecules will be passing through the septum *toward* the sugar solution than are passing in the opposite direction, partly because the baffled sugar molecules, in their attempts to pass through interfere with the free diffusion of the water *from* the sugar side. Besides, the sugar within exerts some attractive or restraining force on the water.

As a consequence, water will accumulate on the sugar side, until the excess hydrostatic pressure or "head" thus built up, by increasing the return diffusion of water, forces an equilibrium. The amount of this hydrostatic unbalance or "head" is termed the *osmotic pressure*, and it is measured by observing the rise of sugar solution (due to increase in its volume by the incoming water), in a tube or manometer into which the solution expands *directly*. Naturally, by exerting this precise counter-pressure, the unequal diffusion of the solvent molecules may be counterbalanced.

The osmotic pressure is proportional to the number of *par-*

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\* This naturally means the untreated, water-permeable variety.

*ticles* per unit volume, and with ideal solutions, the osmotic pressure  $p$  is related to the molecular weight of the solute,  $M$ , by the formula

$$M = (22.4 \times 760) \frac{C}{p} \frac{T}{T_0}$$

where  $C$  = concentration of the solute

$T$  = experimental temperature, in degrees absolute  
(above  $-273^\circ \text{C.}$ )

$T_0 = -273^\circ \text{C.}$ , the absolute zero.

If molecules split into ions, the concentration of *particles* is increased, whereas if there is molecular association or aggregation the number of particles acting is diminished. The kinetic activity of the particles must also change with variation in size. The molecular complexity of a substance in solution depends on its specific nature, its concentration, on the temperature, on the solvent, and often on other factors, *e.g.*, the pH. For further details see the paper of Prof. W. E. S. Turner (University of Sheffield) on "Molecular Association" in Vol. I of Alexander's Colloid Chemistry; also his book on the same topic.

### THE DONNAN EQUILIBRIUM

If solutions of two different salts are separated by a membrane permeable to each salt, and so thin that the ionic separations, referred to just above, cease to be a factor, then (assuming that no untoward chemical reactions prevent) the two salts will distribute themselves equally on either side of the membrane. However, if one of the salts forms a "colloidal ion" which cannot pass through the membrane, a lop-sided diffusion balance may result, which is called the "Donnan Equilibrium," after Prof. F. G. Donnan who first subjected it to mathematical analysis. We may picture the non-diffusible "colloid ions" standing firm, and saying to an equal number of ions of opposite charge (as the French did at Verdun): "They shall not pass!"

In considering the Donnan Equilibrium in addition to the assumption that definite chemical compounds are involved, the following *simplifying assumptions* are also generally made: (1) There is complete dissociation of the solutes on both sides of the membrane; (2) the "colloidal ion" is absolutely non-diffus-

ible; (3) the diffusive activities of the diffusible ions are equal; (4) the membrane is unaffected by changes in concentration of ions, etc.

Obviously, the oppositely charged ions must pass through the membrane in pairs; for otherwise very high electric charges would be built up. Therefore *an equilibrium* will be established when *ionic pairs* are passing the membrane in *opposite directions*, but in *equal numbers*. Since enormous numbers of ions are involved, we may here invoke the laws of probability or chance, just as we do when we figure out the chances of drawing a pair of cards from a pack, or of throwing a pair with dice.

Let us first consider the extremely simple case, where all the salt is dissociated and on one side of the membrane, and where each ion is equally active and diffusible. Suppose that there are five positive and five negative ions (the principle is the same with 500, or 5,000,000, or  $5 \times 10^{20}$  pairs of ions), and that they are moving about at random. What are the chances of a pair of ions meeting in an area of the membrane so small that they may pass through together? Since there are five negative ions, obviously *each* positive ion has *five times* as many chances of finding a mate as it would have if there were only *one* negative ion; and *all* the five positive ions have five times the chance of *one* positive ion. Therefore the chance, or probability, of ionic pairs meeting in this small area will be  $5 \times 5$ , that is, 25 times the chance existing if there were but one ion of each kind present.

Putting this in more solemn language, we may say that *the probability of two events coinciding* (all other conditions being the same and coincidence being possible), is expressed by *the product of the probability of each event occurring in a given period at a certain point*.

Let us apply this extremely simple notion to a diffusion cell (Fig. 12) having *inside* the diffusion thimble a mixture of equal amounts of salt and of Congo red, and outside, in the diffusion vessel, a solution having precisely the same amount of salt at the same hydrostatic level. Let us assume that the dye and the salt are both completely dissociated into positive and negative ions, but that the red dye (which is the sodium salt of a complex organic dye-acid) yields a completely non-diffusible negative ion, whose diffusive activity is so slow compared with the extremely active Na and Cl ions, that we may entirely disregard it. Let

us suppose that the number of positive ions yielded by each dissociating substance to be five (hundreds, billions, or what you will). The number of negative ions is, naturally, also expressed by five, though the actual number is fixed by the concentrations of the salts.

Since the negative dye-acid ion is colloidal and is "counted out," so far as concerns diffusion, we have within the diffusion thimble only 15 ions to consider — 10  $\text{Na}^+$  and 5  $\text{Cl}^-$ . The chance of an  $\text{Na}^+\text{Cl}^-$  combination passing to the outer vessel is, therefore, expressed by  $10 \times 5 = 50$ . But in the outer vessel

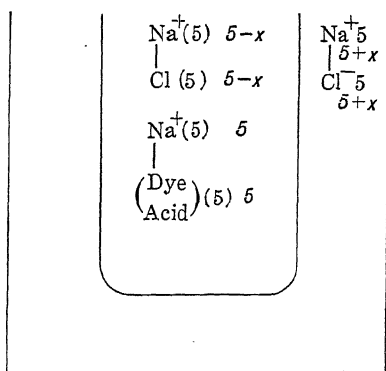


Fig. 12. Diagrammatic representation of the Donnan equilibrium. Initial ionic concentrations in plain type. Ionic concentrations at equilibrium in italics.

we have only 5  $\text{Na}^+$  and 5  $\text{Cl}^-$  ions, so that the probability of an  $\text{Na}^+\text{Cl}^-$  combination passing into the thimble is expressed by  $5 \times 5 = 25$ . Quite evidently the two solutions are not in diffusional balance, for more  $\text{NaCl}$  will be passing out of the thimble than goes in. Therefore the salt concentration within and without the thimble, initially the same, *must become unequal*, and tend to reach an equilibrium or balance of some kind.

We are now somewhat in the position of the minister who said to his congregation: "I have tried by all honest means to complete the fund for our new building. We are now going to see what a raffle will do for us." Therefore let us see what a little very simple algebra will tell us about the conditions which may be expected at equilibrium; that is, when  $\text{NaCl}$  will be diffusing with equal rapidity in either direction.

Designate by  $x$  the number of  $\text{Na}^+$  ions which have, *at equilibrium*, passed from the thimble to the outside vessel. Naturally, the same number ( $x$ ) of  $\text{Cl}^-$  ions will have passed with them; and the concentrations of diffusible ions will be (see Fig. 10) as follows:

Inside of thimble— $\text{Na}^+ = (10-x)$ ;  $\text{Cl}^- = (5-x)$ .

Outside of thimble— $\text{Na}^+ = (5+x)$ ;  $\text{Cl}^- = (5+x)$ .

But since equilibrium is now postulated, the probabilities of ion-pairs passing in opposite directions must be equal; that is,

$$\overset{\text{inside}}{[\text{Na}^+]} [\overset{\text{outside}}{\text{Cl}^-}] = [\text{Na}^+] [\text{Cl}^-],$$

where the square brackets betoken concentrations in the orthodox printed form of the physical chemist. Supplying the equilibrium concentrations given just above, we have the following equation:

$$(10-x)(5-x) = (5+x)(5+x)$$

whence

$$25x = 25, \text{ and } x = 1$$

We will therefore have 8 parts of the total 20 parts of  $\text{NaCl}$  remaining within the thimble, while 12 parts will be outside; that is, 40 per cent. inside and 60 per cent. outside.

Prof. F. G. Donnan points out (Chem. Rev., 1925, 1, 87) that since the equations are based on two assumptions, *viz.*, the existence of equilibrium and of certain restraints restricting diffusion, "the theory will hold equally well whether we have to deal with 'colloid units' which have acquired an ionic character (electric charge) by adsorption of ions, or with simple molecules which have become ionized by the loss or gain of electrons." The unequal distribution of charged particles resulting from the interference with free diffusion, gives rise not only to a difference in concentration, but also to differences in potential (electric charge) and osmotic pressure across the membrane. Donnan points out that in applying to living cells and tissues and their circumnate fluids, the extremely simple relationships resulting from the ideal theory "will represent only a very small part of the associated complex of phenomena which make up the reaction of the cell towards variations in its environment."

## 4. SEPARATIONS

## ULTRAFILTRATION AND ELECTRO-ULTRAFILTRATION

H. Bechhold found that he could make filtering membranes of varying degrees of permeability by forming them from jellies of varying concentration. He used principally collodion dissolved in glacial acetic acid and afterward immersed in water, and gelatin jellies hardened in ice-cold formaldehyde. The jellies were formed and hardened on pieces of filter paper, which were supported from below by nickel wire cloth, and clamped between two flanges. The liquid to be subjected to ultrafiltration

TABLE XIV

Suspensions.
Prussian blue.
Platinum sol (made by Bredig's method).
Ferric oxid hydrosol.
Casein (in milk).
Arsenic sulphid hydrosol.
Colloidal gold hydrosol (Zsigmondy's No. 4, particles about 40 $m\mu$ ).
Colloidal bismuth oxid (Paal's "Bismon").
Colloidal silver (Paal's "Lysargin").
Colloidal silver (von Heyden's "Collargol," particles about 20 $m\mu$ ).
Colloidal gold hydrosol (Zsigmondy's No. 0, particles about 1-4 $m\mu$ ).
Gelatin solution, 1 per cent.
Hemoglobin solution, 1 per cent (molecular weight about 16,000).
Serum albumin (molecular weight about 5000 to 15,000).
Diphtheria toxin.
Protalbumoses.
Colloidal silicic acid.
Lysalbinic acid.
Deuteroalbumoses <i>A</i> .
Deuteroalbumoses <i>B</i> (molecular weight about 2400).
Deuteroalbumoses <i>C</i> .
Litmus.
Dextrin (molecular weight about 965).
Crystalloids.

is introduced in the chamber thus formed and forced through the prepared septum by appropriate pressure, which may run up to 20 atmospheres or more and may be produced by a pump or by compressed gas (air, nitrogen or CO<sub>2</sub>). Table XIV, prepared by Bechhold, shows various colloids arranged in order of the diminishing size of their particles in solution, and was obtained by using ultrafilters of varying degrees of porosity or permeability.

By means of ultrafiltration through ultrafilters of appropriate permeability, not only may colloids be separated from crystalloids, but colloids having particles of different sizes may be separated from each other. An electric current may be used to facilitate the passage of electrolytes and fine colloidal particles through the filter, the process being then termed *electro-ultrafiltration*.

Great care must be used in gauging the size of the pores in ultrafilters. Thus Prof. Richard Zsigmondy in Chapter XIV, on "Filtration Experiments," of his book "Colloids and the Ultramicroscope" (Wiley & Sons, 1909), says:

"All three kinds of filters (Maassen, Pukall and Chamberland) contain pores large enough to allow the passage of gold particles of about 30  $m\mu$  and less. The pores of a cell are of very different sizes, the Chamberland cell containing, for example, large pores, which allow the gold particles to pass through, and others which retain most of them. The size of the pores is, however, not the sole criterion in filter experiments. It is of especial importance in coarse filters, whether the particles to be filtered are held to the surface of the cell by adhesion or "adsorption" (A), or not (B).

(A) In the first instance the substance to be filtered gathers upon the outside surface (and to a certain extent in the deeper pores), and prevents the other particles from forcing their way through; first, because the pores are made smaller; second, because the particles held fast to the surface of the cell repel the freely moving particles following the course of the current.\*

(B) When adhesion or adsorption does not take place, all colloiddally dissolved substances pass freely through the cell, providing the pores are large enough.

In the presence of a protective colloid, *e.g.*, egg albumen, all the gold particles pass smoothly through, whereas in the absence of protectors, matters proceed as in case (A). The fact that protected gold particles of 30  $m\mu$  and over easily pass through Maassen and Pukall filters should be of interest to bacteriologists. The Chamberland filter, too, contains, besides the very small pores chiefly present, others which permit the passage of particles of the size mentioned."

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\* This action may be due to the well-known negative electric charge of the particles, which apparently also affects the adhering gold particles.

Another point of great importance to bacteriologists has been emphasized by Professor H. Bechhold, who found that lecithin emulsions whose droplets were several  $\mu$  in diameter passed through ultrafilters capable of retaining hemoglobin, and whose pores were less than 30  $m\mu$  (pressure 150 g./cm.<sup>2</sup>). Bechhold explains that the droplets assume a filiform shape in their passage, reforming on their exit.\*

Bechhold says in the latter reference, p. 832:

"Therefore the diameter of the pores of the ultrafilter gives no definite idea of the diameter of a retained particle as far as *emulsions* are concerned, whose disperse phase has a low surface tension against the dispersing phase."

Since the work of Heilbronn, Chambers, Seifriz and others shows the great changes in viscosity which micro-organisms exhibit during mitosis, and since changes in the milieu may produce similar changes, we must observe many precautions before hazarding an opinion about size deduced from filtration experiments. Alteration of the pH of the milieu may modify the charges of particle and of filter, and even reverse them. Salt ratios and antagonism must be considered, as well as anything leading to formation of surface films. And these or other factors may influence the viscosity of protoplasm. Professor H. Schade illustrates a phagocyte passing in filiform fashion through an orifice very much less than its average diameter, and appearing in its usual guise after it emerges on the other side of the membrane. (See Alexander, Vol. II, p. 664.)

These facts brought out by Zsigmondy and by Bechhold are frequently overlooked by bacteriologists (See J. Alexander, "Science," 1927, 65, 207; *ibid.* 1933, 77, 449-50). The last named paper indicates that the superior filterability shown by certain bacteria grown in "K" medium (A. I. Kendall, "Science," 1932, 75, 295-301) may well be due to the high protective action of this medium as compared with beef broth medium. Speaking of filterable viruses, Dr. T. M. Rivers (Rockefeller Institute)

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\* See Bechhold's "Colloids in Biology & Medicine," Bullowa's translation, Van Nostrand; also Vol. I of Alexander's "Colloid Chemistry, Theoretical and Applied," Chem. Cat. Co., 1926, articles on Ultrafiltration and Electro-ultrafiltration by Bechhold, and also one by Zsigmondy on a new method of making ultrafilters by blowing air of regulated moisture content on films of cellulose ester solution. The size of the pores in the reticulated "blush" structure formed by precipitation of the cellulose ester depends upon the nature of the solvents, amount of water in the air, etc.



stated (Jordan and Falk's "The Newer Knowledge of Bacteriology and Immunity," 1927, p. 519): "Methods of filtration are crude and inaccurate, and the most any one can say concerning viruses is that under given experimental conditions they either pass or do not pass through certain filters. The failure to pass through a filter, however, is certainly not determined in every instance by the size of the virus."

### SEDIMENTATION

*The Resistance of Fluids to Moving Bodies.* Until Galileo, in 1589, made his classical experiment in the presence of the faculty and the students of the University by dropping weights of various sizes from the leaning tower at Pisa, it had been generally taught\* on the authority of Aristotle that a two pound weight would fall faster than a one pound weight. And so it may, if the shapes of the weights are so designed that the lighter weight offers greater air resistance than the heavier weight. Galileo rightly attributed the small differences observed in the fall of his weights to differences in air resistance. It is only in a vacuum that a feather and a piece of lead fall with equal velocity, and the air pump had not yet been invented.

The method whereby relatively heavy birds are able to float in thin air had also aroused men's curiosity. In the Ambrosiana Library in Milan is a sketch of a projected flying device by that versatile engineer-artist-scientist, Leonardo da Vinci, which he based on keen observations of the wings and flight of birds. The story of Daedalus and Icarus goes back to the time of Minos of Crete and the Minotaur. Many problems of fluid resistance had been solved by nature and by man. Fishes and birds are "stream-lined," and so are spears and arrows; the latter have evenly disposed feathers at one end to establish a balanced air resistance there.

### *Stokes' Equation and Its Application*

Sir C. G. Stokes † developed an equation which expresses the resistance ( $w$ ) offered by a *homogeneous* fluid of viscosity  $\eta$

\* It has been recently pointed out that Galileo had precursors.

† "On the theories of the internal friction of fluids in motion, and the equilibrium and motion of elastic solids," Phil. Mag., 1846, 29, 60-62; Cambr. Phil. Soc. Trans., 1849, 8, 287-319, 1856, 9, 8,

towards the motion within the fluid of a *sphere* of radius  $r$ , moving with a *moderate* velocity  $v$ . Stokes found that

$$w = 6\pi\eta rv$$

and this "law" has been found to hold *if its basic assumptions are maintained*. As previously pointed out (see p. 33), Millikan found that Stokes' law fails to apply to colloidal oil droplets falling in air, because the air is no longer homogeneous relative to such tiny particles. Furthermore, Stokes' law is not applicable when the velocity is high enough to produce eddy current (turbulent as opposed to smooth stream-line flow), or when the moving object is near enough to the walls or bottom of a container of the fluid to influence the result.† At *high* velocities, the resistance to motion through a fluid approximates variation with the *square* of the velocity, which explains why rapidly rotating propellers can move ships and airplanes with good speed, although the same propellers if turning very slowly would be practically without effect.

If precautions are taken to prevent convection currents in the fluid due to shaking or to temperature changes, then particles suspended in the fluid will fall freely under the action of gravity, unless they are so small that their diffusion due to Brownian motion keeps them permanently afloat and in true solution. Since gravity is acting constantly, the rate of fall of the particle will continue to *increase* until the resistance offered by the fluid just balances the downward acceleration due to gravity. Therefore when the rate of fall becomes constant we must have

$$6\pi\eta rv = \frac{4}{3} \pi r^3 (d - d_1) g$$

In the right-hand side of this equation  $\frac{4}{3} \pi r^3$  is the volume of the spherical particle,  $g$  is the acceleration due to gravity (approximately 980 cm. per gram per second), and  $(d - d_1)$ , termed the *absolute density*, is the difference between the specific gravity of the particle ( $d$ ) and that of the fluid ( $d_1$ ), because the particle

\* For the corrections necessary for "wall-effect" and "end-effect," see Ladenberg, Ann. der Physik, 1907, (IV), 23, 9 and 447.

is buoyed up by a force equivalent to the weight of the fluid it displaces.\*

Solving the above equation for  $v$ , we get

$$v = \frac{2(d - d_1)g}{9\eta} r^2$$

Since all the quantities in this equation besides  $v$  and  $r$  are constants, with fixed conditions the steady rate of fall of the sphere ( $v$ ) will vary as the *square* of its radius; and since we can observe  $v$  experimentally, we can calculate the value of  $r$ , which gives us the size of the sphere.

Stokes' equation and its derived forms obviously should not be applied to needles or to thin plates, but they hold quite well for particles which approximate spheres. Sven Odén (Alexander's "Colloid Chemistry," Vol. I, p. 863) proposed the term "*equivalent radius*" to represent the radius of a perfect sphere which *would* fall through the fluid with the same velocity as the non-spherical particle under consideration.

The application of this equation for the steady rate of fall, to water drops falling in air, will clear up the apparent paradox shown by clouds in the sky, where particles of specific gravity *unity* remain floating in a fluid (air) of specific gravity 0.0013. Considering the viscosity of air as 0.00017 poise (the C. G. S. unit), and substituting these values in the equation, we find that water droplets having a radius of 100  $m\mu$  would fall less than half a centimeter per hour. Most cloud and fog particles are larger than 100  $m\mu$ , generally ranging from 14 $\mu$  to 35 $\mu$ . At high altitudes they congeal to ice crystals, which may give rise to halos (see p. 168).

The great convection currents (winds) set up by solar radiation work against sedimentation in the *troposphere*, the turbulent atmospheric layer about 7 miles deep lying directly next to the earth. In the next higher isothermal layer, the *stratosphere*, calculations of physicists, *based upon certain assumptions*, indicate that there might be a gravitational segregation of the gases of the atmosphere, exhibited in the following table taken from the International Critical Tables, Vol. I, p. 393:

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\* This last factor (Archimede's principle) is commonly neglected when weighing objects in air, but it is of importance with bulky objects where accurate results are essential.

TABLE XV  
THEORETICAL CHANGE IN COMPOSITION OF THE ATMOSPHERE

Height	N <sub>2</sub>	O <sub>2</sub>	A	CO <sub>2</sub>	H <sub>2</sub>	He
Sea Level .....	77.08	20.75	0.93	0.03	0.01	.....
40 Kilometers up.....	86.42	12.61	0.22	.....	0.67	0.02
80     "     ".....	32.18	1.85	.....	.....	64.70	1.10
120     "     ".....	0.19	.....	.....	.....	98.74	1.07

Such meager observations as exist, however, indicate that the separation is by no means like that calculated, and that factors other than those assumed must be at work.

These calculated changes in composition must not be confused with the progressive rarefaction of the atmosphere as we ascend in it, due to Boyle's law. The lower the layer, the higher the pressure on it due to the weight of gas above; consequently at lower levels the atmospheric gases, as a whole, are under greater pressure and are more compressed than at higher levels. Air-planes flying at high altitudes have air-compressors to condense the rarefied air sufficiently to give sufficient oxygen for proper combustion of their fuel.

### *Visual Demonstration of the Kinetic Theory*

For many years the Brownian movement, discovered by Robert Brown in 1827, was the subject of scientific investigations which showed that it is *not* due to gravity, surface tension, electric or magnetic forces. Wiener (1863), Exner (1867) and Goüy (1888), among others, suggested that the motion is kinetic. The discovery of the ultramicroscope (1903) aroused renewed interest in the question, and soon Albert Einstein\* developed mathematically a molecular kinetic explanation, saying in conclusion: "May some investigator soon be able to resolve the question here raised, which is so important for the kinetic theory." An almost immediate response was given by The Svedberg† who graphed the displacements of colloidal platinum particles flowing across the field of an ultramicroscope, and found that they cor-

\* Ann. d. Physik, 1905, 17, 549; 1906, 19, 371. A. von Smoluchowski (*ibid.*, 1906, 21, 756) and Langevin (Compt. rend. 1908, 146, 530), reached the same results by different methods.

† Zeit. Elektrochem., 1906, 12, 853, 909; Zeit. phys. Chem., 1910, 71, 571.

respond with the predictions of Einstein's equations for such particles. The paths of the flowing particles appeared as wavy curves as they passed in the ultramicroscope.

That the very active Brownian motion of fine particles is due to the impact of the still finer particles of the dispersion medium, is shown by stirring a few drops of whole milk into half a glass of water, and then locating an ultramicroscopic field with a single fat globule in it. Lively casein particles can be seen to jostle the relatively big fat globule about, like a Gulliver assailed by a swarm of Lilliputians, thus indicating that the irregular Brownian motion of the globule and of the casein particles is due to the still more active, though unseen, molecules of the water and dissolved crystalloids.

Zsigmondy\* had found that a gold sol whose particles average  $38m\mu$  gave a re-dispersible sediment on standing five years. We should therefore expect to find evidence of sedimentation throughout the colloidal range, providing we employ sufficiently delicate means of observation, as was done by Jean Perrin.† Just as van t'Hoff had developed the analogy between gases and dilute solutions of crystalloids, so Perrin demonstrated that in colloidal solutions the diffusion and Brownian motion of the dispersed particles are in accord with the demands of the kinetic theory, and that fairly large colloidal particles sediment according to the law of Stokes.

Perrin and his collaborators placed gamboge and mastic sols ‡

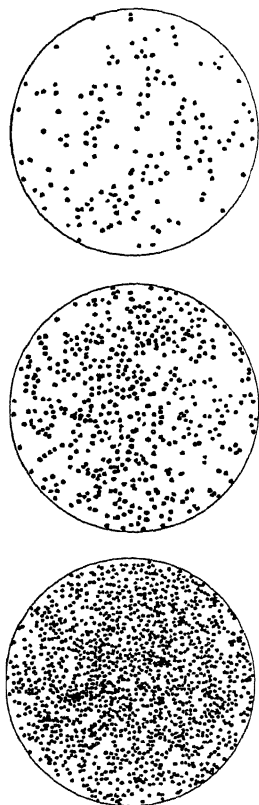


Fig. 13. Sedimentation equilibrium in a mastic emulsion having particles  $1\mu$  in diameter (3 layers  $12\mu$  apart).

\* "Zur Erkenntnis der Kolloide," Jena, 1905; English trans. by J. Alexander, "Colloids and the Ultramicroscope," New York, 1909.

† Bull. soc. franç. phys. 1909, 3, 170; "Brownian Movement and Molecular Reality," 1910; Kolloidchem. Beihefte, 1910, Vol. I, pp. 221-300.

‡ Gamboge disperses spontaneously to a sol in water, probably because of protective colloids present. Mastic sols are made by diluting the clear supernatant portion of a methanol solution of the gum.

in shallow cells on a microscope slide, and *counted the number of particles per unit volume* at successive levels about 10-12  $\mu$  apart. Sols having approximately uniform sized particles were prepared by centrifuging out any large ones, for particles of different sizes settle at different rates of speed, and complications arise because of collisions.\*

The diameters of the particles in Perrin's sols were about half a micron (0.5  $\mu$ ) for gamboge and 1  $\mu$  for the mastic sols. Fig. 13, taken from Perrin's work, illustrates three microscopic fields, 12  $\mu$  apart, in a mastic sol whose particles averaged 1  $\mu$  in diameter.

*Perrin's Law.* Consider a cylinder (see Fig. 13) containing a sol, *e.g.*, of mastic. Perrin found that if the concentration of particles at the bottom be designated as  $C_1$  and the concentration at  $x$  cm above the bottom as  $C_x$ , then

$$\log_e \frac{C_1}{C_x} = \ln \frac{C_1}{C_x} = mgkx \quad (\text{Perrin's law}).$$

where  $m$  = the mass of one particle =  $\frac{4}{3} \pi r^3 \Delta$

$g$  = the acceleration due to gravity = 980

$k = \frac{N}{RT} = 3 \times 10^{13}$  c.g.s. units at normal temperature.

For a *monodisperse sol* (one whose particles are alike in size)  $m$  is a constant; and so, too, are  $g$  and  $k$ . For convenience, represent  $mgk$  by a symbol  $\alpha$ , and use the symbol  $\Delta$  to represent *the absolute density* of the particles ( $d - d^1$ ), that is, the difference between the density of the particle and that of the dispersion medium.

We will then have, for normal temperatures,

$$\alpha = mgk = \frac{4}{3} \pi r^3 \Delta \cdot 980 \cdot \frac{N}{RT} = 10^{17} r^3 \Delta$$

But  $\log_e \frac{C_1}{C_x} = (mgk)x = \alpha x$

Whence  $C_x = C_1 \cdot e^{-\alpha x} = C_1 e^{-x \cdot 10^{17} r^3 \Delta} = \frac{C_1}{e^{\alpha x}}$

\* Where the dispersed particles are lighter than the dispersion medium, *e.g.*, fat in milk, or iron in mercury, they will rise. The smaller the difference in specific gravity between particles and medium, the slower the separation.

where  $e$  is 2.718+, the base of the *Napierian or natural system* of logarithms.\*

This formula indicates: (1) the concentration at  $x$  is some fraction of the concentration below; (2) the value of the fraction (through its denominator) diminishes *exponentially* with both the height ( $x$ ) above the bottom and the value of  $\alpha$ . But  $\alpha = 10^{17} r^3 \Delta$ , so that *its* value increases as the *cube* of the particle radius ( $r$ ) and also as the absolute particle density ( $\Delta$ ). Therefore while particle size is a most potent factor in sedimentation, the densities of both particle and dispersion medium may exert much influence. The following table shows the wide differences in density among common substances (water = 1):

*Dispersed Substance:* Gold, 19.3; Lead, 11.4; Iron, 7.8; Silica, 2.6; Olive Oil, 0.92.

*Dispersing Fluid:* Mercury, 13.5; Bromoform, 2.9; Kerosene, 0.81; Alcohol, 0.789; Air, 0.0013.

With substances *lighter* in specific gravity than the dispersion medium, the value of  $\Delta (= d - d^1)$  will be *negative*, the exponent of  $e$  will be negative, and the value of the fraction  $\frac{C_1}{e^{ax}}$  will be *greater than*  $C_1$ —that is, the concentration above will be *greater* than that below. Such a condition is met with in emulsions of fats and oils in water, where a “cream” layer tends to form (*e.g.*, in milk or in diluted mayonnaise).

TABLE XVI

$\Delta$	=0.01	=0.1	=1.0	=10.0
$\eta$				
0.001.....	12 days	5 days	2½ days	1 day
0.01.....	4 months	50 days	23 days	12 days
0.01.....	3 years	16 months	8 months	4 months
1.0.....	30 years	13 years	7 years	3 years
	$r = 0.3 \mu$	$= 0.1 \mu$	$= 60 m\mu$	$= 30 m\mu$

\* The logarithms in most general use are those of Briggs, the decimal logarithms, having 10 as a base. Where the Napierian logarithm is meant, we write  $\log_e$  or  $\ln$ .

The preceding table of E. E. Ayres, Jr.,\* gives the time calculated to be required for the substantially complete gravity subsidence of particles of various sizes and absolute densities ( $\Delta$ ) in fluids of various viscosities  $\eta$  in c.g.s. units. At the bottom of the table is shown the maximum size of particles still remaining in suspension.

*Water and Air Flotation.* By suspending fine particles in streams of water or of air and gradually diminishing the velocity of the streams, *e.g.*, by passage into containers of larger and larger volume, the water or air currents will permit the deposition of the particles, the finest ones being carried furthest. One of the oldest types of water-separation apparatus is the "cascade" of Nöbel, described by Wolff.† More recent types are those of G. W. Thompson and A. H. M. Andreasen.‡ This method of separation is largely used for separating particles of intermediate size, above colloidal dimensions.

*Brownian Motion as a Factor Opposing Sedimentation.* If water is layered over a crystal of copper sulphate, the gradual diffusion of the salt becomes visually evident. Graham remarked (p. 4) that as regards diffusion crystalloids belong to the more "volatile" class, whereas colloids represent the *comparatively* "fixed" class of substances. The increasingly greater kinetic or Brownian motion of increasingly smaller particles opposes their sedimentation and finally tends to dominate.

*The diffusion constant or specific diffusion rate,  $D$ ,* is the amount of solute diffusing per unit time across a unit area under the influence of a unit concentration difference (Fick). The smaller the size of the dispersed particles, the greater their opportunity to pass through the "holes" in the dispersing medium, which are regulated by the mean free paths of its molecules. It is only with sufficiently large particles having sufficiently hampered kinetic motion in a homogeneous medium that Stokes' law of frictional resistance can be applied. Assuming such large and *spherical* particles, Albert Einstein § calculated the value of  $D$ :

\* Trans. Am. Inst. Chem. Eng., 1916, 9, 203; Alexander's "Colloid Chemistry," Vol. I, p. 857).

† Z. anal. Chem. 1864, 3, 89.

‡ Proc. Am. Soc. for Testing Materials, 1910. Koll-chem. Beihefte, 1928, 27, 401.  
§ Zeit. Electrochem. 1908, 14, 235.



$$D = \frac{RT}{N \cdot 6\pi\eta r}$$

$$\text{whence } N = \frac{RT}{D \cdot 6\pi\eta r}$$

But  $N$  is Avogadro's number, the number of molecules per unit volume, determined by various other methods.

Perrin's observation (*loc. cit.*) on diffusion gave values of  $N$  which check fairly well with other values, and led him to state: "Therefore Einstein's theory establishes the applicability of Stokes' law. It is, then, probable that this law, which I have shown holds for particles down to one tenth  $\mu$ , will also apply to larger molecules whose diameter is less than one thousandth  $\mu$ ."

As The Svedberg\* points out, the combination of centrifugal and diffusion data may enable us to determine the density and molecular weight of larger molecules.

If a well stirred dispersion of tiny particles is poured into a tall sedimentation cylinder (placed in a thermostat to avoid formation of convection currents), on standing the particles begin to settle out and to accumulate toward the bottom. A *density gradient* becomes established which may be measured in several ways: (1) by taking off and testing samples at various heights in the cylinder; (2) by reading off the progressive change in density at a certain level on a manometer connected at that level, *e.g.*, in the instrument described by W. J. Kelly,† or by means of a specific gravity bob attached to the arm of a Westphal balance.

Sven Odén‡ developed a most ingenious sedimentation apparatus, in which the depositing particles are received on the pan of a sensitive balance, and continuously and automatically weighed, the results being simultaneously recorded as a graph. Odén's instrument has been used successfully to study the structure, aggregation and settling of precipitates, the course of coagulations, and many technological, agricultural and geological problems connected with the properties of soils, of foundry sands, the ability of different earth formations to support the foundations of buildings, etc. *Sedimentation analysis* confirmed the

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\* "Centrifugal and Diffusion Methods for the Study of Dispersity and Hydration in Sols" in Alexander's "Colloid Chemistry," Vol. I, pp. 838-854).

† Ind. Eng. Chem., 1924, 16, 928-930.

‡ Alexander's "Colloid Chemistry," Vol. I, pp. 861-909.

important geological conclusions of Baron De Geer (see p. 184) regarding *varves* (laminated clay deposits).

Careful work with various types of sedimentation apparatus developed the importance of two facts: (1) the particles of most dispersions are not uniform in size; (2) particles frequently cohere to make a composite larger particle (primary colloidal particles aggregate to form secondary colloidal particles; see p. 67), and even if thoroughly stirred with the dispersion medium (*e.g.*, water) may fail to deflocculate, or may aggregate or reflocculate again.

These effects are readily shown by stirring a little clay or earth into water and dividing the mixture equally among three glasses. A few drops of ammonia added to one glass will aid deflocculation, while a little alum added to another glass will effect flocculation. The third glass may be kept for comparison.

*Particle Size Analysis.* After considering and describing a great variety of methods, H. Gessner\* indicates the adaptation of the several types of methods as follows:

TABLE XVII

<i>Diameter of Particles</i>	<i>Method Applicable</i>
100 to 0.1 mm.....	Sieving
0.1 to 0.01 mm.....	Water flotation or Sedimentation
0.01 mm to 1 $\mu$ .....	Sedimentation
Smaller than 1 $\mu$ .....	Centrifugation, Colloid-chemical methods

## CENTRIFUGATION AND ULTRACENTRIFUGATION

*Centripetal and Centrifugal Force.* A body moving with *constant* velocity in a *straight* line has no acceleration in any direction. However, if we wish to *force* this body to move in a circle, we must change its direction continuously at a constant rate; the force required to do this is called the *centripetal force*, for it *pulls* the body towards the center of rotation.

But by virtue of its *inertia*, the particle offers *resistance to deflection* which is termed the *centrifugal* force because it tends to make the body *fly* away from the center of rotation. This shows itself in the centrifugal pull which one feels on whirling a weight attached to a string. The string exerts the centripetal force.

\*"Die Schlamm-Analyse," Leipzig, 1931, p. 154.

In dealing with centrifuges it is more convenient to describe the motion in terms of *angular velocity* (speed of rotation), represented by the symbol  $\omega$ . And the centrifugal force ( $f$ ) exerted on a particle of mass  $m$  is  $f = m\omega^2x$ , where  $x$  is the distance of the particle from the center of rotation. Since the mass equals volume ( $4/3\pi r^3$ ) times the absolute density ( $\Delta$ ), we have

$$f = \frac{4}{3} \pi r^3 \Delta \omega^2 x, \text{ where } r \text{ is the particle radius.}$$

Now in all practical cases where centrifuges are used the particles are suspended in some fluid which offers *frictional resistance* to the "fall" of the particles under the urge of centrifugal force. If the fluid is homogeneous relative to the size of the particles and the kinetic activity of the particles is not too great, Stokes' law applies. When the centrifuge reaches a steady velocity, any particle whose distance from the center of rotation is  $x$ , will quickly acquire a uniform velocity ( $v$ ) toward the periphery. In a tiny time ( $dt$ ) the particle will move outward a tiny distance ( $dx$ ). Hence its velocity (distance/time) is

$$v = \frac{dx}{dt}$$

Substituting this in Stokes' equation, we have for the resistance of the fluid ( $w$ )

$$w = 6\pi r \eta \frac{dx}{dt}$$

which may be equated against the centrifugal force it just balances. That is,

$$6\pi r \eta \frac{dx}{dt} = \frac{4}{3} \pi r^3 \Delta \omega^2 x$$

Whence

$$v = \frac{dx}{dt} = \frac{2r^2 \Delta \omega^2 x}{9\eta}$$

If we integrate between an initial position ( $x_0$ ) of the particle and a subsequent position ( $x_1$ ) after the lapse of time  $t_0$  to  $t_1$ , we get

$$\int_{x_0}^{x_1} \frac{dx}{x} = \frac{2r^2\Delta\omega^2}{9\eta} \int_{t_0}^{t_1} dt$$

$$\ln \frac{x_1}{x_0} = \frac{2r^2\Delta\omega^2 t}{9\eta}$$

whence

$$r = \sqrt{\frac{9\eta \ln(x_1/x_0)}{2\Delta\omega^2(t_1 - t_0)}}$$

Where a sol contains particles all of one size,  $x_0$  is the position of the boundary between sol and supernatant liquid at time  $t_0$ , and  $x_1$  the position at time  $t_1$ . With very fine-grained sols which demand prolonged centrifuging, diffusion of the particles causes a more or less pronounced blurring of the boundary, and must be taken into account.

The Svedberg developed an *ultracentrifuge* which has produced sedimentation forces over half a million times the force of gravity. The specimens are placed in tiny tubes held within a rotating head or rotor which is spun in a very low pressure atmosphere of hydrogen (a "hydrogen vacuum") at speeds approximating 75,000 revolutions per minute (1250 turns per second).\* The rotor is run by an oil-driven turbine, and the temperature of the oil and the whole apparatus is carefully regulated to avoid disturbing convection currents.

Svedberg (see, *e.g.*, Chemical Reviews, Feb. 1934; Kolloid, Zeit., 1934, 67, 1-16; Science, 1934, 79, 327-332) states that the theory is fairly simple as long as we have to deal with electrically neutral molecules, *e.g.*, proteins at their isoelectric point. If the sedimenting molecules are dissociated, the heavier portion is held back by the electrostatic attraction of the lighter ions, an effect which may be counteracted by the addition of a non-sedimenting electrolyte, *e.g.*, KCl. The following two types of measurement may be made:

#### (1) *Sedimentation Equilibrium Method.*

By whirling the specimen until an equilibrium is reached between sedimentation and diffusion, we can see if there is only one

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\* Much higher rotational velocities have been obtained, but the rotors are apt to explode under the high centrifugal force developed.

or more than one molecular species. If several kinds of molecules are present and their weights are sufficiently different, they may be separated. For each molecular species, the following formula is applicable:

$$M = \frac{2RT \ln(C_2/C_1)}{(1 - V\rho)\omega^2(x_2^2 - x_1^2)}$$

where  $M$  = molecular weight

$R$  = ideal gas constant

$\rho$  = density of solvent

$V$  = partial specific volume of solute

$\omega$  = angular velocity

$C_2$  and  $C_1$  = concentrations of solute at distances  $X_2$  and  $X_1$ , respectively, from the axis of rotation.

The value of  $V$  is found pycnometrically, from the following formula:

$$V = \frac{w - (l - h)}{\rho h}$$

where  $w$  = weight of solvent in pycnometer

$l$  = weight of the solution in pycnometer

$h$  = weight of solute in pycnometer

$\rho$  = density of solvent.

## (2) *Sedimentation Velocity Method.*

By using centrifugal fields of sufficient strength, we may cause different molecular species to sediment with measurable velocities, obtaining for each species its *sedimentation constant*,  $S$ , from the following formula:

$$S = \frac{dx}{dt} \cdot \frac{1}{\omega^2 x} \cdot \frac{\eta}{\eta_0} \cdot \frac{1 - V\rho_0}{1 - V\rho}$$

where  $dx/dt$  = observed sedimentation velocity

$x$  = distance from center of rotation

$\eta$  = viscosity of solvent

$\eta_0$  = viscosity of water

$\rho_0$  = density of water (at 20° C.)

and the other symbols have the same meanings as given under Method (1) just above.

If  $M$  is found by Method (1) and  $s$  by Method (2) the molar frictional constant,  $f$ , is given by the formula:

$$f = \frac{M(1 - V\rho)}{s}$$

But the molar frictional constant of a sphere  $f$ , according to Stokes' law, would be

$$f_0 = 6\pi\eta N \left( \frac{3MV}{4\pi N} \right)^{\frac{1}{3}}$$

If, therefore, the ratio  $\frac{f}{f_0}$  is unity, the molecules in question are spherical, any deviation from spherical shape running the value above unity. The ratio  $\frac{f}{f_0}$  has been termed the *dissymmetry constant*.

*Air-driven Centrifuges ("Spinning-top" type).* Henriot and Huguenard † described an air-driven spinning top for obtaining very high rotational speeds. This type of apparatus has been developed into an extremely powerful and inexpensive ultracentrifuge by Prof. J. W. Beams and his collaborators ‡ (University of Virginia) and by Prof. James W. McBain and his collaborators § (Stanford University).

McBain states (*loc. cit.* Nature) that any good mechanic can make the simple stator and hollow rotor for about \$10 to \$15, and that with much less air pressure than is available in an ordinary garage, the top may spin at several thousand revolutions *per second*, producing centrifugal forces of the order of one million times gravity. As Svedberg had already found, it is difficult to get metal that will withstand the enormous centrifugal forces developed at these high speeds. Pickels and Beams (Science, 1935) have made a further improvement by suspending the rotor from the air-driven spinning top on a short length of piano wire, and enclosing it in a vacuum chamber. A rotor of duralumin exploded when the speed went just above 2,200 rev. per

\* Compt. rend. 1925, 180, 1389; J. de Phys. et Rad., 1927, 8, 443.

† Beams, Rev. Sci. Inst., 1930, 1, 667; Beams and Weed, Science, 1931, 74, 44; 1933, 78, 338-40; J. W. Beams and E. G. Pickels, 1935, 81, 342-3; J. Chem. Phys. 1934, 2.

‡ J. W. McBain and C. M. O'Sullivan, J. Am. Chem. Soc., 1935, 57, 780; J. W. McBain, Nature for May 16, 1935.

second, and to maintain this speed it took, per minute, only 12 cubic feet of air (measured at normal temperature and pressure), supplied to the spinning top at 70 lbs. per sq. in. The lineal peripheral speed was over 2,000 ft. per second.

McBain reports (*loc. cit.*) an observation of the sedimentation constant ( $S$ ) of mercuric chloride of  $8.90 \times 10^{-13}$  as compared with theory  $8.91 \times 10^{-13}$ . The respiratory protein of the blood of the earthworm at 2020 r.p.s. and  $22.5^\circ$  gave  $S = 72 \times 10^{-13}$ . One per cent of KCl was present and the protein was monodispersed (one size of protein particle). The extensive work of Svedberg and his collaborators on proteins, etc., is referred to on p. 300.

## 5. SOLS AND GELS

### PECTIZATION AND PEPTIZATION

*Pectization.* Briefly stated, pectization means the coagulation of a colloidal sol, and peptization its redispersion. If a small quantity of an electrolyte is added to a pure ruby red colloidal gold solution, the latter changes to a blue or violet color, and deposits its gold as a fine blackish coagulum or precipitate. By watching in the ultramicroscope the coagulation of very dilute milk by dilute acid, the individual particles of the colloidal casein may be seen to gather gradually together into groups, whose motion becomes progressively less as their size increases, until they are no longer able to stay afloat, and finally coagulate in large grape-like clusters. Hardy believed that the particles of colloids adsorb the oppositely charged ions of electrolytes present; at the *isoelectric point* (that is, when there is no excess either of positive or negative charges on the particles) coagulation occurs. If, however, an *excess* of electrolyte be added *all at once*, the isoelectric point may be passed before coagulation occurs, and the particles acquire a charge opposite to the one they had originally. Under such conditions, no coagulation may result.

Burton epitomizes the difference in action of various electrolytes on hydrophobe sols as follows: "Two remarkable results are evident on comparing the coagulative powers of various electrolytes on colloids of different kinds; first, the coagulation depends entirely on the ion bearing a charge of sign opposite to that of the colloidal particle; and, second, with solutions of salts,

trivalent ions have, in general, immensely greater coagulative power than divalent ions, and the latter, in turn, much greater than univalent. Acids and alkalis in particular cases act more strongly than the corresponding salts."

In some cases a coagulum may be redispersed by washing out the flocculating salt. In other cases a small amount of alkali or acid is needed after the washing, to give the particles a suitable charge. In most cases where water is the dispersion medium the dispersed substance is stabilized by a negative charge; so that the  $\text{OH}^-$  ion (ammonia, caustic soda or potash, soda ash, silicate of soda, tri-sodium phosphate) is a successful peptizer. Too much cannot be used, for then precipitation will again ensue. Thus clay deflocculated by alkali, is flocculated by an excess.

The *salting-out* of the dispersed phase of *hydrophile colloids* by relatively high concentrations of *neutral* salts appears to result from the superior attraction of the salt for the water, that is, to be a solubility effect. Hofmeister and his pupils (Lewith, Arch. Exptl. Path. Pharmacol., 1888, 24, 1; Hofmeister, *ibid.*, 1888, 24, 247) found that solutions of egg white were rendered turbid by smaller concentrations of citrates than of tartrates, sulphates, chlorides, etc. The precipitation capacity of various anions fell into the following series:

Citrate > tartrate > sulphate > acetate >  
nitrate > chlorate.

This is known as the *Hofmeister or lyotropic series*. The highly soluble iodides and thiocyanates do not produce turbidity in ordinarily obtainable concentrations, and they follow the chlorates in the series. The influence of cations is much less marked. Hofmeister's results showed

$\text{Li} > \text{K}, \text{Na} > \text{NH}_4 > \text{Mg}$

The presence of acidity or of alkalinity ( $\text{H}^+$  or  $\text{OH}^-$  ions which are extremely active), may obscure the lyotropic series. For the evidence in the controversial questions centering about the lyotropic series and the Donnan equilibrium, the reader is referred to various papers in Alexander's "Colloid Chemistry," and to treatises mentioned in the bibliography.

High-tension electric discharges may also effect the coagulation or precipitation of a finely subdivided or dispersed phase;



which fact was utilized by Sir Oliver Lodge in dispelling fogs, and by Cottrell in coagulating smelter and similar fumes.

*Peptization.* So strong is the analogy between digestion and colloidal disintegration that Thomas Graham, the father of colloid chemistry, coined the word *peptization* to express the liquefaction of a gel. He first speaks of the coagulation or pectization of colloids. "The pectization of liquid silicic acid," he states, "and many other liquid colloids is effected by contact with minute quantities of salts in a way which is not understood. On the other hand, the gelatinous acid may be again liquefied, and have its energy restored by contact with very moderate amounts of alkali. The latter change is gradual, 1 part of caustic soda, dissolved in 10,000 water, liquefying 200 parts of silicic acid (estimated dry) in 60 minutes at 100 degrees. Gelatinous stannic acid also is easily liquefied by a small proportion of alkali, even at the ordinary temperature. The alkali, too, after liquefying the gelatinous colloid, may be separated again from it by diffusion into water upon a dialyzer. The solution of these colloids in such circumstances may be looked upon as analogous to the solution of insoluble organic colloids witnessed in animal digestion, with the difference that the solvent fluid here is not acid but alkaline. Liquid silicic acid may be represented as the 'peptone' of gelatinous silicic acid; and the liquefaction of the latter by a trace of alkali may be spoken of as the peptization of the jelly. The pure jellies of alumina, peroxide of iron and titanin acid, prepared by dialysis, are assimilated more closely to albumen, being peptized by minute quantities of hydrochloric acid."

Peptization is in reality deflocculation, a dispersion of groups into separate particles which once more acquire active motion and remain afloat or in solution. The detergent action of soap and dilute alkalis is largely due to the fact that they deflocculate adhering particles of "dirt."

*Viscosity.* Viscosity depends largely on the relation between kinetic motion and free or specific surface. It may be measured by time of flow from an orifice under a fixed head or pressure (Ostwald or Engler types of viscosimeters), or by measuring the force needed to shear layers of liquid past each other (Couette or MacMichael types). Crystalloid solutions exhibit low viscosity; the rapid motion of their particles aids flow. The relatively coarse suspensions are likewise not viscous, because of

deficiency of free active surface. In the colloidal zone we find maximum viscosity, which falls off on either side (zone of maximum colloidity, see p. 35 *et seq.*).

Slowly moving particles exhibit inertia to the commencement of flow, and this accounts for what is known as "plasticity" or "yield value" of viscous materials. Theoretically everything should have some yield value, though in many cases it is not measurable, especially over limited time,\* and with relatively slow rates of flow.

*Viscosity* is really internal friction, and may be defined as the resistance of a substance to shear or flow. The standard of viscosity is the *poise* (named after J. L. M. Poiseuille, the French physicist), and is represented by the Greek letter *eta* ( $\eta$ ). It is the tangential force required to maintain a velocity of 1 cm. per second between two planes each 1 cm<sup>2</sup> and 1 cm. apart. The *centipoise* is  $\frac{1}{100}$  of a poise.

*Fluidity* measures the tendency to flow, and is the reciprocal of the viscosity. It is represented by the Greek letter *phi* ( $\phi$ ), and therefore  $\phi = \frac{1}{\eta}$ .

*Plasticity*. Fluids flow under the smallest conceivable shearing stress, *e.g.*, by virtue of their own weight, and continue to do so. On the other hand, there are many substances where external pressure must be applied before flow begins. The force, *f*, required to start such *plastic flow* (as distinguished from *viscous flow*), is termed the *yield value*.

Yield value represents the force required to convert a static system into a moving or dynamic system. This change involves the breaking of bonds between the constituent particles of the static system, either along selective planes of slip or cleavage, as with metals under pressure (*e.g.*, tin and lead); or else in all directions, as with the thixotropic systems described below, in

\* See J. Alexander, "Glue and Gelatin," p. 98 *et seq.*

Thomas Graham said (Proc. Roy. Soc. Lond., 1864): The ultimate pectization of silicic acid is preceded by a gradual thickening in the liquid itself. The flow of liquid colloids through a capillary tube is always slow compared with the flow of crystalloid solutions, so that a liquid transpiration-tube may be employed as a colloidoscope. With a colloidal liquid alterable in viscosity, such as silicic acid, the increased resistance to passage through the colloidoscope is obvious from day to day. Just before gelatinizing, silicic acid flows like an oil.

which case we have a deflocculation accompanied with marked increase of Brownian motion. If the bonds between the particles reestablish themselves, the yield value will reappear, in whole or in part; that is, thixotropy will again be evident.

*Mobility* with plastic flow is somewhat analogous to fluidity with viscous flow; it is the reciprocal of the stiffness, and is represented by the Greek letter *mu* ( $\mu$ ).

The subjoined diagram (Figure 14) indicates that the slope

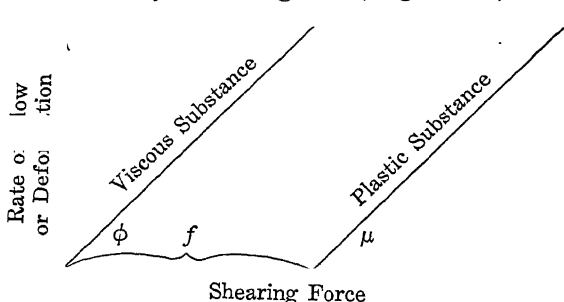


Fig. 14.

of the graph for viscosity represents the fluidity,  $\phi$ , and the slope of the graph for stiffness represents the mobility,  $\mu$ ; for the smaller are these angles, the greater is the effect.

Plasticity is obviously a complex property, for it involves both yield value  $f$ , and mobility,  $\mu$ .\*

### SOL-GEL TRANSFORMATION

Consider conditions existing in a cooling gelatin solution. As the temperature falls and thermal agitation diminishes, the finely dispersed gelatin particles are reduced in their kinetic activity (Brownian motion) and their mutual attractive forces begin to assert themselves, leading to the formation of *secondary colloidal particles* (groups of the *primary colloidal particles*), which, with gelatin, are elongated or thread-like especially if the solution is sufficiently dilute. As the chains grow and become tangled in each other, the viscosity (internal friction) increases, until finally the whole of the fluid is enmeshed in the growing tangle or else becomes part of it. The sol has become a gel. C. R. Smith (J. Am. Chem. Soc., 1919, 41, 135-150) found a marked difference between gelatin dried at above 35° and gelatin dried below 15°. A colloid substantially free from volatile dispersion medium is termed a *xerogel*.

\* My thanks are due to Prof. E. C. Bingham (Lafayette College) for critical suggestions.

By using powdered karaya gum (a kind of insoluble Indian tragacanth which swells greatly in water), the growth of viscosity with the swelling of the gum particles may be followed by the eye, if gum of about 80 mesh is used (about 2% gum to 98% water). As the gum particles hydrate and swell, not only do they spread out and interfere with each other, but the amount of *free water*, (which acts as a separator or "lubricant" between the particles), steadily diminishes. The viscosity therefore increases, and with higher concentrations of gum a jelly is formed, which is plastic. (For further details, see J. Alexander, J. Am. Chem. Soc., 1921, 43, 434-440).

### THIXOTROPY

Certain weak gels may be fluidified by comparatively slight stirring or shaking. The phenomenon was termed *thixotropy* by Freundlich and Peterfi, from the Greek meaning *to change by touching*. von Kuhne (Virchow's Archives, 1863, 26, 222) had noted that when a nematode (thread-like worm) worked its way through a muscle cell, its movement seemed to liquefy the striations; but they set again after the worm passed on. Szegvari and Schalek (Kolloid-Zeit., 1923, 32, 318, and 33, 326) describe the formation of a thixotropic gel by treating concentrated ferric oxide sol with a small amount of electrolyte, *e.g.*, NaCl. Similar alumina sols can also be made (Buzagh, Kolloid-Zeit., 1929, 47, 223). Rubber latex (stabilized) can be made thixotropic by adding a small amount of aluminum sulphate. Certain kinds of bentonite (see p. 199) exhibit the phenomenon, as do also finely ground Solnhofen slate (lithographers' stone) and dry starch mixed with cold water to make a "mud." The protoplasm of living cells (*e.g.*, amoeba) flows, and sets, and flows again, during life; but on death an irreversible gel forms.

### AGEING

When a sheet of dry gelatin is heated above 120° for a while, it becomes insoluble in water, although it still swells to a certain extent. Apparently its constituent particles have approached so closely that the attraction they have for water can no longer suffice to force them apart. As gels stand, they often develop such a close approach of their particles, that a clot is formed, and fluid is squeezed out and exuded, while the clot shrinks. This

is known as *syneresis*. A common instance is milk-curd. As we grow older, our muscles and other tissues tend to become less hydrous and flexible because of ageing phenomena. There is a steady loss in *percentage* of water in the body, from the time of birth. All this is beautifully illustrated in the statue by Gian Bernini (Borghese Gallery, Rome) representing Aneas carrying from burning Troy his old father Anchises, and leading by the hand his young son Ascanius. The virile muscles of the stalwart Aneas contrast with the plump, turgid tissues of the child and the shriveled and shrunken tissues of the old man. The young sculptor, then but 15 years of age, was assisted in this work by his father, Pietro.

## 6. SWELLING AND SHRINKING

Where the attraction of the constituent particles of a dried colloid gel (their idioattraction, as Graham termed it), is not too great, immersion in water or often mere exposure to water vapor results in the entry of water between the particles, its absorption and adsorption. The result is that the gel swells. Glue or gelatin are typical examples.

The force with which water is attracted is almost incredible. Thus when a ship carrying a cargo of soya-beans sprang a leak, the hull was split asunder as the beans swelled. When the great obelisk was being erected in the Piazza of St. Peter's (Rome), Pope Sextus V ordered complete silence under pain of death so that the engineers would not be disturbed at their formidable task—the monolith weighs many tons. The blocks and falls raised the huge stone as far as they could, but it was still not settled on its base, and the engineers were in consternation. Suddenly a sailor, Brescia of Bordighera, roared out: "*Aqua alle funi!*" (Wet the ropes.) This was done immediately, and as the fibers of the ropes swelled, the ropes shortened sufficiently to seat the stone. As a reward, Brescia and his descendants received the right to supply palms to St. Peter's on Palm Sunday.

A very old farmers' custom, going back no doubt to antiquity, is to use dried hardwood wedges to split big stones. A number of small holes are drilled along the line where the split is desired, and into these holes are driven the dried hardwood wedges. On wetting the wedges, the stone is split by the force of their swelling.

On the other hand, use is made of the shrinking of colloid structures. In framing pictures, it is usual to moisten the paper backing before gluing it out on the frame. As the paper dries, it contracts and shrinks, drawing to a drumhead tightness. The furrier and shoemaker wet their skins and leathers and then pin or nail them out as desired, so that on drying they draw into the proper shape or form.

## HYSTERESIS

The term *hysteresis* (from the Greek *hysteresis*, to lag behind) was introduced by J. A. Ewing, who defined it (Phil. Trans. 1885, 176, 524) thus: "When there are two qualities M and N such that cyclic variations of N cause cyclic variations of M, then if the changes of M lag behind those of N, we may say that there is *hysteresis* in the relation of M to N. For example, if an iron bar is subjected to a magnetic field which rises to a maximum and then diminishes, the magnetization of the bar at any given field-strength, will be less on the rising side and greater on the descending side, because the iron tends to keep its magnetization, probably because of the *reluctance* of its constituent particles to respond perfectly and instantaneously to the field changes." In electrical machinery (generators, transformers) where certain iron parts undergo many reversals of their magnetic fields per second, this causes an energy loss which heats up the metal. Very pure iron (total carbon 0.0003% or less) and a nickel alloy (permalloy) show small hysteresis losses when properly heat treated. On the other hand, for permanent magnets alloy steels containing chromium, tungsten, etc., are used.

Jakob Maarten van Bemmelen (Z. anorg. Chem., 1897, 13, 234; see also his collected works, "Die Absorption," Dresden, 1910, p. 230 *et seq.*) upon plotting the graphs showing the differences the taking-up and loss of water by gels, especially of silicic acid, noted their similarity to the magnetic hysteresis curves and said: "These phenomena have a certain similarity with the so-called hysteresis in physics, *e.g.*, with the magnetization and demagnetization of iron. . . . It does not seem inappropriate to apply the term *hysteresis* to this phenomenon shown by the hydrogel of silicic acid, *i.e.*, the lag in the change of (water) content behind the change in pressure."

Van Bemmelen also found that the properties of the gels altered with time (ageing), with the mode of formation and treatment (past history) of the gels, and stated that this "lability" indicates the existence of as yet unknown factors.

The microscopic and ultramicroscopic structure of silicic acid gels were investigated by Zsigmondy and his pupils (see "Kolloidchemie," Leipzig, 1912, p. 145 *et seq.*). Zsigmondy said (p. 160) that apparently the radii of the tiny menisci in the capillaries of the gel are larger on rehydration than on dehydration, but that the lesser amount of hydration on rehydration might be due to adsorption of air. The vapor pressure of liquids evaporating from such concave menisci is smaller than in the case of a plane surface (W. Thompson (Lord Kelvin), Phil. Mag., 1881, (4), 42, 448). On the other hand, as Prof. Herbert Freundlich (Univ. of London) points out ("Colloid and Capillary Chemistry," 1922, H. S. Hatfield's trans., p. 664), changes in the structure of the gel itself must produce changes in the size of the capillary openings. Besides this, the closer approach of the constituent gel units increases the strength of their union (see p. 83 and 86), so that it is more difficult to separate them again. The physical condition of the adsorbed water is also a factor.

L. Arisz (Kolloid-chem. Beihefte, 1915, 7, 1-90) made extensive experiments with gelatin and gelatin gels, which show that their behavior is also dependent on their past history; and Prof. R. A. Gortner (Univ. of Minnesota) and W. F. Hoffman (Proc. Soc. Exp. Biol. and Med., 1922, 19, 257-64) J. Phys. Chem., 1927, 31, 464) reported similar conclusions. Thin gelatin sheets are usually dried out from more dilute solutions than thick sheets, and take up more water on swelling. Perhaps this is why "thin-cut" glue and gelatin is preferred by some, apart from more ready solubility. (See J. Alexander, "Glue and Gelatin," 1923, p. 89.)

Hysteresis phenomena are closely related to "ageing," which is of great importance in biological matters. (See p. 147; also Prof. R. A. Gortner, "Outline of Biochemistry, 1929, p. 53).

## 7. COLLOIDAL PROTECTION

Without an understanding of the underlying principles, isolated facts have long lain like individual gems scattered or even lost in the wide fields of human experience. A theory is necessary to string them together, each in its proper place, to form a

beautiful necklace; or, rather, a theory to serve as a matrix that forms of them a cutting drill, with which we may bore into the hard rocks of the still unknown.

Continually, throughout chemical and technological literature, the use of protective substances crops up, only to be buried again or to be hidden in the *oubliette* of some "secret" or rule-of-thumb formula. The *aurum potabile* of the alchemist was made by reducing gold chloride in the presence of ethereal oils. Then followed the use of solutions of tin which stabilized the gold sol by the stannic oxide simultaneously produced, giving the rich purplish solution known as the purple of Cassius (see p. —). In 1794 colloidal gold produced *in situ* was known as a dye for silk; in 1821 egg-white, isinglass, and starch were used as protectors for gold sols; and the *Lehrbuch* of Berzelius (1844) contains several recipes for producing gold sols of various shades. In 1856 Faraday \* reports the discovery of jelly (evidently isinglass or gelatin) as a protector to colloidal gold; and, finally, Zsigmondy (1898), then unaware of the preceding work, rediscovered gold sols.†

Thomas Graham was probably the first to recognize colloidal protection, as such. (See Zsigmondy, "Colloids and the Ultramicroscope," p. 43.) In his paper on diffusion (see Chapter II), Graham describes the dialysis of crude caramel, obtained by heating raw sugar to 210-220° C. a colored substance diffuses away, leaving behind the portion richest in carbon, which, in 10 per cent solution, is gum-like and forms a weak water-soluble jelly. When thoroughly dry this dialysis residue can be heated to 120° C., and still remain completely soluble; but it becomes insoluble if evaporated to dryness on a water-bath. Both the soluble and the insoluble caramel have the same empirical formula,  $C_{24}H_{15}O_{15}$ .‡ The liquid caramel is quite tasteless, neutral in reaction, and is extremely sensitive to crystalloid reagents. Traces of mineral acids, alkali salts, and alcohol make it pectous; the precipitated caramel yields a brownish-black powdery substance, insoluble in hot or cold water. Graham then states: "The presence of sugar and of the intermediate brown substances protects the liquid caramel in a remarkable degree from the action of crystalloids, and

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\* *Phil. Trans.*, 1857, p. 145.

† "Colloids and the Ultramicroscope," 1909.

‡ We would now write  $H_{30}$  instead of  $H_{15}$ .



accounts for the preceding properties not being observed in crude caramel."

In dilute potash the pectous caramel becomes gelatinous and dissolves again on heating. Caramel is 600 times less dialysible than sodium chloride (ordinary table salt), and 200 times less than sugar. Referring to the analogy between caramel and anthracite coal, Graham states: "Caramelization appears the first step in that direction—the beginning of a colloidal transformation to be consummated in the slow lapse of geological ages."

A most important contribution of Zsigmondy, however, was his demonstration that stable though highly sensitive gold sols could be made without the use of protectors provided the presence of coagulators was avoided, and also the proof that these sensitive sols could be stabilized by the addition of gelatin, gum, and the like. Then only did the full import of colloidal protection begin to dawn and the use of the principle, as such, begin to be understood and developed. Zsigmondy also synthesized the purple of Cassius by simply mixing the pure colloids of gold and stannic acid, thus proving that here the stannic acid takes the part of a protector.

Von Meyer and Lottermoser \* had just previously re-discovered protective action as such, calling attention to the fact, long utilized by practical photographers, that albumin stabilizes silver sols. Lottermoser † later said that "on the addition of very stable colloids, as albumin, gelatin, agar, or gum arabic, to a silver sol, no precipitation is caused by electrolytes until the stable colloid is coagulated. The less stable silver sol is thus protected against the electrolyte by the more stable colloid; it becomes more like the latter in its behavior."

### *Gold Number*

With his pure but sensitive ruby-red gold sols (gold content about 0.005 to 0.006 per cent), Zsigmondy then established the relative protective value of a number of protective substances. The "gold figure," compiled from the results of Zsigmondy and Schryver (see below), indicates the number of milligrams of protector which just fail to prevent the coagulative color change

\* *J. prakt. Chem.*, 56 (1897), 241.

† "Anorganische Kolloide," 1901, p. 50.

from red to violet of 10 cc. of the colloidal gold solution upon the addition of 1 cc. of 10 per cent sodium chloride solution. It must be remembered that the relative protective values were determined with gold, and while they are generally maintained, they may be different with other substances, especially those that coagulate the protector or adsorb it poorly. A substance fixed by adsorption often does not behave as it does when free, so that stability and protective power are not necessarily parallel functions.

Substance	Gold Number
Gelatin.....	0.005 to 0.01
Russian glue.....	0.005 to 0.01
Isinglass.....	0.01 to 0.02
Casein (in ammonia).....	0.01
Egg-globulin.....	0.02 to 0.05
Ovomucoid.....	0.04 to 0.08
Glycoprotein.....	0.05 to 0.1
Amorphous egg-albumin.....	0.03 to 0.06
Crystallized egg-albumin.....	2.0 to 8.0
Fresh egg-white.....	0.08 to 0.15
Gum arabic.....	0.5 to 4.0
Gum tragacanth.....	2.0 $\pm$
Dextrin.....	6.0 to 20.0
Wheat starch.....	5.0 $\pm$
Potato starch.....	25.0 $\pm$
Sodium oleate.....	0.4 to 1.0
Sodium stearate at 100 degrees.....	0.01
Sodium stearate at 60 degrees.....	10.0
Deutero-albumose.....	$\infty$
Cane sugar.....	$\infty$
Urea.....	$\infty$
Stannic acid sol (cld).....	$\infty$

### *Classification of Sols (see p. 55)*

Zsigmondy, following W. B. Hardy, classified colloid sols into two broad classes, based on their behavior on desiccation—the reversible or resolvable, and the irreversible or irresolvable sols. These correspond roughly with the groups hydrophile-hydrophobe (Freundlich), lyophile-lyophobe (Perrin), and suspensoid-emulsoid (Wo. Ostwald). Although some salts (citrate, sulfocyanates) may act as protectors, protection is generally accomplished by adding a reversible or emulsoid colloid to an irreversible one, which thereupon acquires reversible properties—that is, it becomes insensitive to electrolytes, redissolves after desiccation (at any temperature that does not render the protector insoluble), and passes through ultrafilters that would otherwise hold it back.

The generally accepted explanation of this phenomenon is that advanced by Bechhold,\* that the protector is adsorbed at the free surfaces of the protected particle. Zsigmondy supports this view, although he was unable to detect ultramicroscopically any sign of the adsorbed layer or any diminution in the Brownian motion due to an adsorbed surface layer. This is not surprising, as the protecting layer is probably only one or a few molecules thick. Another possibility is that the protector, following its adsorption, may change the net charge of the particles.†

Experimentally, it is a most surprising fact that certain minimal quantities of protectors actually sensitize instead of protect, and may themselves even produce flocculation. Thus, according to Bechhold,‡ 0.0003 to 0.0001 parts of gelatin per million will flocculate gold sols or oil emulsions. The work of J. Billiter § indicates that this is due to the fact that in such cases the minute amount of added protector brings the other colloid to or near the isoelectric point, where, as Hardy has shown, all colloids are especially susceptible to coagulation.

From what has been said it is evident that although, in general, oppositely charged colloids precipitate each other, if an excess of a positive protective reversible (emulsoid) sol is quickly added to a negative irreversible (suspensoid) sol, the protector is adsorbed and protects before precipitation can occur. If, however, only a very small quantity of the protector is used, or, what amounts practically to the same thing, if the protector be added very slowly, precipitation may occur before protection can be established—that is, precipitation may depend upon the speed of mixing as well as on the relative proportions mixed. This gives us also an explanation of the curious Danysz phenomenon (Ann. Pasteur, 1902, 16, 331).

It would be a long task to discuss the numerous cases where colloids are used, wittingly or unwittingly, in scientific, medical, or technical practice, as protectors, deflocculators, and emulsifiers; or where they must be removed because their presence is detrimental. Problems of this kind abound in such widely diverse

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\* *Z. phys. Chem.*, 48 (1904), 385.

† Millikan ("The Electron"; also Alexander, Vol. 1, p. 181) was able to have colloidal droplets of oil, mercury, etc. "capture" as many as 150 electrons. All "charges" therefore, are not necessarily due to chemical "ions."

‡ "Colloids in Biology and Medicine," translated by J. G. M. Bullowa.

§ *Z. phys. Chem.*, 51, (1905), 142.

fields as photography, metallurgy, brewing, rubber, paper, glass, filtration, cooking, cement, agriculture, tanning, paints, pharmacy, biology, etc. Colloidal sols exist everywhere in the organism, and no reaction takes place there without being influenced by their presence.

To illustrate the working of protection, compare precipitates of silver chloride and tin or lead "trees" made in the presence and in the absence of gelatin, or divide a lead acetate solution into three parts, adding a little hot gelatin solution to the last. The first will give with hydrochloric acid a curdy precipitate of lead chloride; the second will give with sodium chloride (which is less highly ionized than HCl) a turbid lead chloride sol; while the gelatin-containing solution will, preliminarily at least, show no visible turbidity with sodium chloride.

Simple colloidal protection has long been known. Let us now consider some newer aspects of this remarkable phenomenon—namely, double or plural protection, autoprotection, and cumulative protection.

#### DOUBLE OR PLURAL PROTECTION

In 1908, while experimenting with milk, it seemed to the author that casein might be an adsorption product containing protein and calcium salts. Accordingly, an attempt was made to produce a colloidal precipitate of calcium phosphate in the presence of such protectors as gelatin and gum arabic. The protector was added first to the sodium phosphate alone and then to the calcium chloride alone; but in neither case could a precipitate be obtained which approached casein in fineness or stability.

Upon following mentally the course of the formation of colloidal calcium phosphate in the body, the idea was conceived that, since in the organism *all* reacting fluids hold protectors, perhaps the result could be obtained by adding some protector to *both* of the reacting solutions. The experiment was at once tried, and yielded, with gelatin as protector, a colloidal calcium phosphate which could be precipitated by both acid and rennin. Upon emulsifying some olive oil in the mixture, a stable artificial milk was obtained. Thus was developed the principle of double or plural protection, for which a U. S. patent was secured. (U. S. P. No. 1,259,708.)

The literature contains several instances where this principle has been used in a more or less empirical manner. These were found subsequent to taking the patent. Thus, Carey Lea produced some of his colloidal silver by the following formula:

Solution 1	Solution 2
Water.....800 cc.	Water.....800 cc.
20 per cent Rochelle salt solution.....200 cc.	20 per cent Rochelle salt solution.....200 cc.
40 per cent silver nitrate solution 50 cc.	30 per cent crystalline ferrous sulfate solution.....107 cc.

Solution 2 was then added to Solution 1. The Rochelle salt here acts as a protector.

In the photographic field the so-called Lippmann "grainless" emulsion is made by the following formula:

Solution 1	Solution 2
Gelatin.....75 grains	Gelatin.....75 grains
Potassium bromide.....3 grains	Silver nitrate.....45 grains
Water.....8 oz.	Water.....8 oz.

The ingredients are mixed in the order given; and after allowing the gelatin to swell, the solutions are heated to 95° F. Then Solution 2 is added to Solution 1. Prof. S. R. Cajal (Madrid) estimated that in Lippmann emulsions which will register all colors up to violet, the grain size *after development* approximates 0.02 to 0.05 $\mu$ , that is, 20–50  $m\mu$ . (Smithsonian Report, 1907, p. 240, "The Structure of the Lippmann Heliochromes.")

Lobry de Bruyn\* found that, upon adding gelatin to both reacting solutions, precipitation may in many cases be inhibited, a colloidal dispersion resulting. Thus, under these conditions potassium bichromate and silver nitrate give a brick-red coloration but no precipitate. In general, Lobry de Bruyn used 0.1 to 0.05 *N* solutions, protecting them with 5 to 10 per cent of gelatin.

The value of this principle in producing colloidal precipitates is obvious, especially for colors, insecticides, pharmaceutical preparations, etc. It is also of the highest importance in biology and medicine, and may serve to explain many anomalies in physiology, pathology, and related branches, where things hap-

\* *Rec. trav. chim.*, 19 (1900), 236; *Ber.*, 35 (1902), 3079.

pen *in vivo* that are not duplicated *in vitro*. Almost no reactions occur in the organism which are not controlled by the protective colloids everywhere present.

## AUTOPROTECTION

Many substances are naturally prone to assume the colloidal state, and in a large number of these it appears that the molecular aggregates first reaching the colloidal degree of dispersion where surface forces predominate, adsorb the less aggregated groups or isolated molecules, and thus the advance toward visible crystallization is delayed, or, for all practical purposes, entirely inhibited. Such a condition occurs in sulfur and also in pure iron, where one allotrope,  $\gamma$ -iron, seems to be adsorbed by  $\alpha$ -iron (ferrite). Ammonium salts, in particular, and some oleates exhibit the phenomenon. The globulitic stage is often a precursor to crystallization, but conditions may prevent emergence from this stage. Lactose acts this way. Several remarkable cases of autoprotection have been reported and these will be briefly considered.

W. B. Hardy\* found that 5-dimethylaminoanilino-3, 4-diphenylcyclo-1, 2-dione, upon cooling from its solutions in organic solvents, gives gels that gradually become crystalline. Gortner and Hoffman† report that dibenzoyl-L-cystine forms even in 0.2 per cent solution a rigid gel, which in the course of several weeks crystallizes almost completely. So powerful is its gelatinization that this dilute solution makes as strong a jelly as a 5 per cent solution of gelatin. Camphorylphenylthiosemicarbazide acts similarly, its solutions in organic solvents forming, on quick cooling, gels that gradually become crystalline.‡

## CUMULATIVE PROTECTION

The general rule in colloidal protection is that anything which removes, coagulates, or destroys the protector, or disperses it crystalloidally, will cause the protected dispersion to coagulate. Thus, on adding ferric chloride to olive oil emulsified with gum arabic, the gum is coagulated and loses its emulsostatic action,

\* *Proc. Roy. Soc. (London)*, 87A (1913), 29.

† *J. Am. Chem. Soc.*, 43 (1921), 2199.

‡ Forster and Jackson, *J. Chem. Soc.*, 91 (1907), 188; E. Hatschek, *Kolloid Z.*, 11 (1912), 158.

so that the oil separates out—the emulsion “breaks.” On the other hand, anything that protects the protector—that is, stabilizes it against coagulation, crystalloidal dispersion, or destruction—will tend to stabilize the protected sol. Thus, some ammonia in a gelatin-protected sol would tend to prevent the coagulation of the gelatin by formaldehyde, and an antiseptic would prevent its dispersion by bacteria or enzymes which, as the work of E. Zunz indicates, may convert protectors into coagulants. The rennin coagulation of milk may be of this nature, the enzyme converting the protective lactalbumin into a coagulant.†

This introduces a new idea—*cumulative protection*. In many cases we must expect to find that the protector of the protective colloid is itself a colloid, and there is no reason to doubt that cumulative protection may extend through a series of several colloids, or colloids and crystalloids, giving a structure which, like a house of cards, may collapse if any one of its essential supports is removed.

This aspect of protection does not seem to have been recognized or investigated experimentally as such, and it offers a wide field for research. As instances of its practical operation may be mentioned glasses, alloys, and the gluten of wheat and rye flours. Many protein and similar complexes may be built up in this fashion in the course of the series of orders of aggregation which Nature exhibits between the truly molecular congregation of atoms and the emergence of visible particles.

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† Alexander, *8th Intern. Cong. Appl. Chem.*, 1912.

## CHAPTER IX

### PRACTICAL APPLICATIONS OF COLLOID-CHEMICAL PRINCIPLES

THE practical applications of colloid chemistry are so manifold and widespread that they touch every branch of science and technology. Whole books may be and have been written on many of the most restricted fields, while the scientific literature teems with monographs and articles, directly on, or applicable to, colloid-chemical subjects. In what follows, it will be possible therefore to give not an exhaustive, but only a most general survey, intended primarily to show the ubiquity of colloid phenomena; and many important topics must be dismissed with a most rudimentary discussion, altogether incommensurate with their importance.

Practically all the substances we meet with in our everyday life are colloids, and we are mainly colloids ourselves. The foods we eat, the clothes and shoes we wear, the wooden furniture we use, the houses we live in with their windows, carpets and floors, the metals and rubber of our automobiles as well as their leather or leather substitutes, the very books and newspapers we read, and the paper and twine that our purchases come wrapped in—all are largely if not entirely composed of colloids, that is, of matter in the colloidal condition. Consequently, problems in colloidal chemistry appear in every branch of science, industry and technology.

It is intended here to give in outline a sketch of a number of these applications, stressing more particularly those that have biological and technological bearings, but including others that show the operation of the colloid-chemical principles involved. In order to bring some coherence into this extensive survey, the topics are gathered into more or less related groups as follows:

- I. Astronomy; Meteorology; Aerosols (Smokes, Fogs, Dusts); Chemical Warfare; Perfumes, Odor, and Taste; Geology; Mineralogy; Gems.



- II. Agriculture; Soils (Genesis and Classification); Clays; Ceramics and Refractories; Flotation.
- III. Dyeing; Shower-proofing Fabrics; Nitrocellulose; Celluloid; Explosives; Paint, Pigments; Varnishes; Emulsions.
- IV. Soaps and Detergents; Adhesives; Lubrication; Coal; Colloidal Fuel; Petroleum; Asphalt; Fire-Foam; Insecticides.
- V. Filtration; Sewage Disposal; Photography; Brewing; Tanning; Rubber; Plastics; Resins.
- VI. Foods and their Preparation; Baking; Milk; Ice Cream; Confectionery; Gelatin and Glue.
- VII. Glasses; Metals and Alloys; Iron and Steel; Electrodeposition of Metals; Polishing and Surface-flow (the Beilby Layer); Boiler Scale.
- VIII. Chemical Analysis; Photometric Analysis (Colorimetry and Nephelometry); Chromographic Analysis; Pharmacy and Therapeutics; Antiseptics and Germicides.
- IX. Carbohydrates; Proteins.
- X. Biology and Medicine (see p. 324 for subdivisions).

#### ASTRONOMY

As matter in colloidal state is so common on our relatively minute earth, it is but natural to expect to find many instances of colloidal dispersion in the immensity of the Universe.

Cosmic dust is widely distributed throughout space, and as it is gathered up by the superior attraction of the larger heavenly masses (suns, planets, etc.), which in any system grow at the expense of the smaller masses, fresh quantities are continually produced by the collisions of bodies in space, as well as the disintegration of meteorites, comets, asteroids, etc., and perhaps also by radiation of subatomic particles, which later aggregate.

According to Isabel M. Lewis of the U. S. Naval Observatory, a swarm of meteors or "shooting stars" (which are quite different from the large meteorites or fire balls) consists of minute dust-like particles which for the most part do not weigh as much as a single grain. If we could view them outside our atmosphere, they would appear as a cloud of dust reflecting the sunlight, their luminescence being caused by the friction of their

rapid passage through our atmosphere. Particles of colloidal size, which probably accompany them through space, tend to be retarded by the viscosity of our atmosphere.

According to E. H. Vestine of the Canadian Meteorological Service, the *noctilucent clouds* about 80 km (about 49 miles) high, formerly thought to be volcanic dust, are clouds of meteoric dust which reflect the sunlight long after the general twilight has ended. ("Science," 1934, 79, 98.) The *gegenschein*, a faint patch of light on the ecliptic directly opposite the sun, is due to particles concentrated "in a sort of dynamic whirlpool about a point nearly a million miles outside the earth's orbit (C. C. Wylie, *Science*, 1927, 66, 593).

The zodiacal light also seems to be consequent on a cloud of colloidal matter generally believed to surround the sun. Lars Vegard advanced the view that the upper atmosphere contains minute crystals of frozen nitrogen, to which he attributed the blue color of the sky, as well as the green color of aurora borealis. (See *Philosophical Transactions*, Oct. 1923.) This view was later modified by Prof. J. C. McLennen (University of Toronto), who showed that the green aurora color is due to a mixture of helium and oxygen.

The "Planetesimal Hypothesis" of Chamberlin and Moulton (see paper by Prof. W. D. MacMillan in Alexander's "Colloid Chemistry," Vol. I, p. 447) is replacing the Laplace theory of nebular rotation to account for the formation of the solar system, even though the latter was bolstered up for a while by Helmholtz' "contraction theory" to account for solar radiation. This indicated that the sun still had only about 20,000,000 years of "life." However, geological and astronomical evidence indicated that the sun must be much older than Helmholtz' view would permit. The view advanced by Chamberlin and his co-workers is in essence this:

About ten or twenty billion years ago, our sun, then quite similar to what it now is, was "side-swiped" by another passing star, which may in fact have passed many millions of miles away, but still near enough to tear loose from the sun, in a pulsating fashion, enormous masses of matter. Part of this was carried off by the visiting star, part fell back into the sun, and part remained scattered throughout the area of our present solar system,

where, in the slow course of time, the larger masses gathered or "swept up" the smaller ones, forming our planets and their satellites. The meeting of two stars, while rare, becomes a certainty if long enough periods of time are considered, and the age of our galaxy runs into *eons*, an eon being a million billion ( $10^{15}$ ) years. The pulsating nature of the "tides" raised in our sun may account for the orderly nature of our planetary distribution. This view accounts for the fact that our planets all revolve in one direction, and it furthermore allows for the persistence of colloiddally dispersed residues, as well as "captured" matter. The retrograde moon of Jupiter is probably a "captured" satellite.

Heavenly bodies must occasionally meet in collision, and the terrific impact must add to the nebulous or cometary masses of colloidal matter which are distributed throughout space.\* While most of these bodies are self-luminous, others are lighted up by neighboring suns. Light itself is invisible, but a beam of sunlight shot into a darkened room becomes evident by illuminating the innumerable motes in our atmosphere, most of which are colloidal. Some of these atmospheric nuclei, as C. T. R. Wilson has shown, are due to the deposit of moisture, etc., on ions or ionized particles, but others are without charge.

A few years ago when, as astronomers had foretold, the earth was about to pass through the tail of a comet, our yellow journals warned us to prepare for the end—but no one, not even the astronomers, noticed the slightest effect. The tail, whose length ran into millions of miles, was only a vast cloud of colloiddally dispersed extremely tenuous matter, and its luminosity was analogous to the "beam" which a searchlight or automobile headlight shoots through the atmosphere, especially if it is slightly hazy. The spectroscope indicates that the luminosity of the tail is due to reflected sunlight.

The tails of comets seem to consist partially, and the nuclei and coma largely, of colloiddally dispersed matter. The great comet of 1882 which made a transit of the sun was invisible against the solar disc (a position corresponding to attempted

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\* In contradistinction to phenomena of such magnitude Prof. R. A. Millikan (Nobel prize winner) weighed the electron by catching these minute individual particles of negative electricity on colloidal oil droplets which he viewed by an ultramicroscopic device.

observation of colloidal particles in the ordinary microscope against a luminous background), but became visible again after passing beyond the sun's disc (a position corresponding to successful observation of the same colloidal particles in the ultra-microscope against a dark background, the eye of the observer being protected from the source of illumination).

Halley's comet in 1910 had a tail which gave the spectrum of reflected sunlight; but most tails show the spectra of  $N_2$  and CO, while CN and C do not seem to extend beyond the head. Apparently we have still much to learn as to the formation of chemical compounds and molecular aggregates under the conditions of temperature and electronic turmoil which obtain as a comet approaches the sun.

The streaming of the cometary tails away from the sun may be due to the ionization of the constituent colloidal particles, and their consequent electrical repulsion. With colloidal particles the Brownian or kinetic motion is a factor to be reckoned with. J. Clerk Maxwell pointed out (1870) that the intensity of the action of the sun's rays on a particle depends upon its *surface*, which varies as the *square* of its diameter, whereas the gravitation of the same particle to the sun depends upon its *mass*, which varies as the *cube* of its diameter. Theoretically in the case of a particle whose density equals that of water, the repulsion balances gravitation when the diameter reaches 0.0015 mm. ( $= 1.5 \mu$ ). As the diameter diminishes, the repulsive force gains the ascendancy, soon reaching a maximum and again diminishing, until when the particle has a diameter of only 0.00007 mm. ( $= 70 m\mu$ ) the two forces again balance each other.\*

These figures, which refer to a substance having the density of water, are approximately of colloidal dimensions; but in the case of denser bodies the subdivision would be even more profound. It is therefore not surprising that, when the earth recently passed through the tail of a comet, no disturbance of any kind was noticed. The comet's tail is a vast celestial camouflage—its luminosity a macroscopic Faraday-Tyndall effect. From what is stated above we should imagine that in some cases the

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\* See Simon Newcomb's article on "Comet," *Encyclopedia Britannica*, 11th edition. Also Svante Arrhenius, "Worlds in the Making," Harper & Bros. For computation of radiation pressure for free atoms and molecules, see W. Baade and W. Pauli, Jr., *Naturwissenschaften*. 1927, 15, 49.

tail of a comet may point toward the sun, providing that its particles are of the proper size, and in fact Baade's comet, recently visible, showed this phenomenon. Comets have been seen with tails pointing both towards the sun and away from it. Prof. N. T. Bobrovnikoff (Ohio Wesleyan University) informs me that heliocentric or anomalous tails are very exceptional, but were observed in Comets 1844 III, 1862 III, and 1882 II. According to Bredichin, such tails are responsible for meteoric streams.

"In 1909, Debye (Ann. d. Phys., 30, 57-136) made a more extensive analysis of radiation pressure than had been made by Schwarzschild. He based his analyses upon the classical theory of radiation and upon the Lorentz electron theory, and he reached the same conclusion as did Schwarzschild, *viz.*, that on particles of the dimensions of gas molecules the radiation pressure of sunlight would be insignificant as compared with the gravitational attraction." (Fernando Sanford, "Science," 1927, 65, 44). Sanford also quotes the work of De La Rue Stewart and Loewy (Phil. Trans., 1869, 70, and Phil. Trans., 1870) to indicate that sun spots are influenced by planetary configurations, the influence being possibly in the nature of electrostatic induction. Assuming that the planets to be charged to the same potential (since the actual charges are unknown), he estimates the relative planetary effects as follows: Mercury, 6.5; Venus, 2.6; Earth, 1; Mars, 0.16; Jupiter, 0.08.

## METEOROLOGY

What we commonly call "weather conditions" are largely dependent upon the degree of dispersion of water in the atmosphere, and this dispersion is mainly effected and maintained by solar heat and electrical charges. When air carrying water vapor is chilled by rising to a higher level (which means reduced pressure and expansion), meeting a colder mass of air, or even by the alternation of night and day, the moisture it contains assumes the colloidal state as cloud, fog or mist; and as the coagulation of the dispersed water proceeds, these in turn may condense still further into dew, rain, snow or hail, depending upon conditions.

When steam under pressure blows off into the atmosphere, it appears clear some distance from the point of issue and does not become visible until it has condensed into colloidal dimen-

sions. Then as its particles condense still further to drops (or else evaporate or are dispersed), it becomes invisible once more. White cloud particles are already larger than strictly colloidal size.

An interesting exhibition of the principles mentioned is found in the Hawaiian Islands, where the warm, moisture laden trade winds, blowing steadily from the northeast, are caused to ascend by the high volcanic mountains they encounter. As the air ascends, the diminution of pressure causes expansion; the expansion results in cooling; and the cooling leads to deposition of moisture on nuclei (dust, ions, etc.) in the atmosphere, evidenced in the formation of thick clouds at the higher mountain tops and heavy rains there and in the upper valleys. As the air passes on over the mountains and descends to lower levels on the other side, the process reverses itself, and the clouds tend to melt away. A newcomer at Honolulu (locally a *malihini* or tenderfoot) seeing threatening clouds on the nearby hills, tucks an umbrella under his arm. But an old-time resident (*kamaaina*) takes no heed, for he knows that at most only some windblown sprinkles called locally "liquid sunshine," will reach the city.

"You frequently see a streamer of cloud many hundred yards in length drawn out from an Alpine peak. Its steadiness appears perfect, though a strong wind may be blowing at the same time over the mountain head. Why is the cloud not blown away? It is blown away; its permanence is only apparent. At one end it is incessantly dissolved, at the other end it is incessantly renewed: supply and consumption being thus equalized, the cloud appears as changeless as the mountain to which it seems to cling. When the red sun of the evening shines upon these cloud-streamers they resemble vast torches with their flames blown through the air." (Sir John Tyndall, "The Forms of Water in Clouds and Rivers, Ice and Glaciers," 1872). A "plume" seven miles long has been reported as streaming from Mt. Everest (1936).

Rear Admiral Richard E. Byrd (National Geographic Magazine, Aug. 1930, J. Alexander, "Science," 1930, 72, 478), among many other curious physico-chemical phenomena in the Antarctic, refers to the ready formation of finely dispersed (presumably colloidal) ice in the following words:

"It was amazing to see fogs at these temperatures. The air holds a very small amount of moisture at 50 below, but when the

wind stirs the warmer and the colder air condensation of this minute amount of moisture occurs and a real fog is evolved. . . . Even a book lying against a cold wall steamed like a tea-kettle when opened in a slightly warmer atmosphere. When a man stood inside the entrance to one of the house tunnels, the vapor formed by his breathing was so heavy the house appeared to be on fire." Water in the form of colloidal ice seems to be the cause of so great an effect from so small a quantity.

Capt. A. W. Stevens (Nat. Geog. Mag., May, 1936) reports that at great heights the balloon ropes appeared larger and had a phosphorescent glow, apparently due to the effect of the sunlight on water particles escaping from the ropes because of reduced pressure. Under these conditions colloidal ice was probably formed. Their second ascension reached a height of 13.71 miles, and a photograph taken shows the curvature of the earth as well as the division between the troposphere and the stratosphere.

As the water particles in a cloud aggregate, the total specific or "free" surface diminishes, but must continue to hold the total electric charge because the charge distributes itself superficially. This means that the charges on the outside of the individual droplets increase enormously until the lightning discharge occurs.\* We have all noticed how a nearby lightning flash is promptly followed by an increased fall of raindrops whose condensation gave it birth. The condensation of the moisture particles usually shows itself by the cloud assuming a dark gray or bluish-black shade.

Many water droplets are formed about ions or electrons and carry an electric charge. As the droplets aggregate the charge accumulates on the outer surface, so that in a large cloud, with an enormous number of droplets, very high potentials may result. Indeed if the aggregation of the water droplets is not sufficient to obscure the sky, and the charges are very numerous, we may have a "bolt out of the blue"—not an uncommon phenomenon.

*Ball or globular lightning*, though comparatively rare, has been very frequently described. Arago said that the balls "seem

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\*It is possible that in the gymnotus and other "electric fish," an aggregation of colloids in their special glands, due to nervous influences, may underlie the high potential and shock. The brain, even during sleep, emits electric impulses, and these are greatly increased in frequency and intensity in the course of voluntary action. (See section on Bioelectricity.)

to endure for many seconds; they occupy time and have a progressive motion." Admiral Chalmers (Phil. Trans. Roy. Soc., 46, 366) reported that while on H. M. S. Montague (74 guns) on Nov. 4th, 1749, he saw a ball of blue fire, large as a millstone, rolling along the water about three miles to windward. On reaching 40 yards from the main chains, it rose perpendicularly with a fearful explosion and shattered the main top-mast to pieces. Ball lightning appears to have much in common with the globular brush discharges described by Gaston Planté (Comp. rend., 1875, *et seq.*) which sometimes form wandering globular sparks. Planté pointed out that ball lightning involves the same principles as are shown in the globular arcs ("The Storage of Electrical Energy," trans., pp. 151-172, London, 1887), and stated: "Although an aqueous surface is not indispensable for forming luminous electric globules, since we have obtained them over a metallic surface, the presence of water, or of vapor from water, at least facilitates their formation or tends to give them more volume because of the gases furnished by the decomposition of water at high temperature." According to J. C. Jensen (Physics, 1933, 4, 374) ball lightning occurs most frequently in connection with dust, *e.g.*, from a fire-place or in a wind-squall or tornado; and Cawood and Patterson (Nature, 1931, 128, 150) produced laboratory *aerosols* which showed much resemblance to this phenomenon.

The "ball" seems to consist of highly charged and incandescent matter which may be whirled by winds or electro-magnetic fields, the mutual repulsion of the similarly charged particles tending to stabilize it. When the charge is earthed, coagulation ensues, which, if sudden enough, results in a loud report as air rushes in to fill the partial vacuum. The explosive effects often reported seem also to involve an oxyhydrogen explosion, which would be all the more violent if conditions are such as to produce Langmuir's "atomic hydrogen" and perhaps also atomic oxygen.

We do not know to what extent electrical conditions on the earth affect the dispersion of substances in its atmosphere; but since half of the earth is always heated by the sun while the other half is cooler, thermoelectric currents are continually circulating about the earth. Variations in solar radiation, due to sun-spots and the like, cause violent electric and magnetic storms which are intimately connected with the aurora, and other atmospheric phenomena (ionization, electrical charge of dispersed particles).



The C. T. R. Wilson *cloud-chamber* is a device for making visible the paths of alpha particles shot out by radium at speeds approximating 10,000 miles per second, leaving behind them a trail or "wake" of ionized gas molecules. The bottom of the cylindrical chamber is a piston bearing a wet cloth or bit of blotting paper, which moves up and down rapidly. As the piston goes down, the air in the chamber is greatly cooled, and moisture is deposited on each ionized particle in the trail, making the string of them visible as a bright streak against a dark background on sidewise illumination. What appears to the eye as a continuous streak, is really a string of very tiny droplets, brought into visibility by the ultramicroscope-like mode of illumination.

Colloidal ice often occurs at high levels\* and may be the cause of halos, perihelions and periselenes ("sundogs" and "moon-dogs"), etc. In many elevated regions (Idaho) there occur frost fogs called by the Blackfoot Indians "pogonip" or "white death," where finely divided ice, like hoar-frost on a gigantic scale, deposits on trees in huge masses, and is a contributing cause of pneumonia.

Since changes in barometric pressure must affect the CO<sub>2</sub> tension of the blood and tissues, and since this means a variation in the turgidity of the body colloids which incidently affects the circulation and pressure on nerves (see p. 398), we have here one basis for the popular impression that the "weather" influences our feelings. Other factors are of course at work (*e.g.*, evaporation of water from the skin, etc.), but physicians know that with persons suffering from neurotic and rheumatic affections (*e.g.*, arthritis), the effects of weather conditions are noticeable. Change of altitude may have a similar effect.

A typical expression of the ancient folk-notion as to the effect of weather conditions, was given by Dean Swift:†

"A coming shower your shooting corns presage,  
Old aches will throb, your hollow tooth will rage."

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\* Captain Stevens and Lieutenant Johnson of the United States Army, on reaching an altitude of 39,000 feet in an airplane, reported a temperature of 76° F. below zero, and "that the ice particles were visible by the billions, hanging in mid-air, their reflections seeming to form caves." The steamer "Asphalion," arriving at Baltimore, Md., Oct. 31, 1931, reported passing through a "sea of milk." The facts stated indicate that the milkiness was due to a very fine foam.

† From "A Description of a City Shower. In Imitation of Virgil's Georgics," by Jonathan Swift.

The blue color of the sky is caused by diffraction of the sunlight by the earth's atmosphere. Were it not for this gigantic Faraday-Tyndall effect the sun would appear to us as a fiery ball set in a black star-sprinkled sky. The varying shades of bodies of water ("blue Mediterranean," "green" ocean, black, yellow, white, red rivers, etc.) are largely due to the diffraction caused by finely dispersed substances. When we look through a great length of the atmosphere, distant objects such as mountains seem to have a blue tone.

'Tis distance lends enchantment to the view,  
And robes the mountain in its azure hue.

So the poet Thomas Campbell beautifully puts it in his "Pleasures of Hope." Local weather prophets set great store by the appearance of the "hills". Though atmospheric gases exercise some effect, without colloidal dust we would have less romantic twilight, and darkness would fall rather sharply as the sun sinks below the horizon.

After the sun has sunk below the horizon of the Lybian or the Sahara Deserts, an observer in the Nile Valley sees in the west a broad bright band about thirty degrees up, which persists for about three quarters of an hour. The writer has personally observed this, and is informed by Mr. I. H. El Kordi, Chief Radio Engineer of the Egyptian Government, that the same phenomenon is seen over the Arabian Desert. This luminous band appears to be a Faraday-Tyndall effect due to fine dust particles floating at high altitudes, as an aftermath of sand-storms.

The blue-whiteness of snow, which sometimes even assumes a positive blue tint, is due to the reflection of light from its interior surfaces, the color being a structural one. [See J. Alexander, *Science*, 41, 465 (1920.)] Artists generally paint snow, especially the shadows, in blue tones. As Bancroft has pointed out, the blue color of many birds' feathers is due to their colloiddally fine structure. A certain green tree toad owes its color to a structural blue, which on passing through a layer of yellow oil droplets in the skin appears green. If preserved in alcohol, which dissolves out the oil, the toad turns blue.

The tremendous explosive eruption of the volcano Krakatoa in 1883 projected colloidal dust and ashes so high that they gradually spread entirely around the earth. Besides causing glorious

"golden sunsets," such fine dust is by many believed to exert a noticeable influence upon weather conditions. While many particles in such dust greatly exceed colloidal dimensions, it must be remembered that the effects of fine subdivisions do not end abruptly with the usual colloidal limits of 5 to 100 millimicrons. Test plates taken in an airplane, show that pollen grains are numerous at an altitude of 15,000 feet (Hay fever).

The daily papers of February 23, 1929, reporting on the blizzards sweeping Europe, state that black snow fell at Ruschuk, the phenomenon being attributed to volcanic dust. Red dust from the Sahara has caused "bloody" rains and snows. On April 26-27, 1928, Lemberg reported a heavy shower of mud, attributed by Profs. Arctowski and Stenz to dust blown from the arid soil of southern Russia. They estimate that 1,500,000 tons of dust fell in Poland alone.

One more curious function of colloidal atmospheric dust must be mentioned. As Kendall has shown, the proper functioning of the thyroid gland depends upon the presence of a small quantity of thyroxin, an iodine-containing organic compound. This means that iodine must be found in traces in the soil, from which most food directly or indirectly comes. The original source of iodine is the sea, and although some of it exists in geological deposits of sea salt, a continual source of supply to the soil is to be found in the colloidal sea-salt dust, which forms from the ocean's spray and is carried thousands of miles inland before being washed down by the rain. The incidence of goiter and cretinism (largely due to iodine insufficiency) is most marked in interior mountainous (Switzerland, Idaho, Wyoming) regions where the least amount of sea-salt dust is apt to be carried and retained in the soil. Thus it would take a person 1,000 years to drink enough of the water of Lake Superior to give the iodine needed for his thyroid gland.

Goiter was, of course, known in ancient times, and is mentioned by Pliny, the Roman encyclopedist, who died 79 A.D. in a great eruption of Vesuvius. The use of burnt sponge as a goiter remedy was common from the latter part of the 13th century, and was probably based on much earlier folk-lore. In 1812 Courtois discovered iodine, and in 1819 Dr. Coindet of Geneva tried it as a remedy for goiter. He walked into LeRoyer's Pharmacy there, and asked J. B. A. Dumas (then only 18 years

of age) to determine for him if sponge, and especially burnt sponge, contains iodine. When Dumas reported that it did, "Dr. Coindet no longer hesitated to consider iodine as a specific against goiter." (A. W. von Hofmann, *Berichte*, 1884, 17, 637 ref.).

### AEROSOLS—SMOKES, FOGS AND DUSTS

Fogs, mists, and clouds, whether of water or dust, exercise a potent influence on terrestrial climate, flora and fauna, for they govern to a considerable degree the amount of solar radiation reaching the earth's surface. According to one theory, glacial periods were, in part at least, due to such influences.

From a study of the weather records for the past three centuries, Dr. W. J. Humphreys (U. S. Weather Bureau) found that cool cloudy summers followed periods of explosive volcanic eruptions. The great eruption in 1815 of Tomboro (Sumbawa Island, East Indies), which killed 12,000 persons, was followed by the famous "year without a summer," 1816. Here the amount of lava was estimated at six cubic miles; but this sinks into insignificance compared with what must have occurred in earlier geologic times. For example, Prof. Wilbur A. Nelson (U. of Va.) estimates that a prehistoric eruption of a volcano in Tennessee during the Cretaceous period, spat up over 50 cubic miles of material which formed clay-like beds of bentonite that can still be traced 450 miles north and south of the old volcanic site, and 350 miles east and west.

On April 11th, 1932, a large number of volcanoes in the Chilean Andes burst into activity, the ash mantling the pampas of Argentina, covering Buenos Aires with a powdery white blanket in which children made "snow" patterns, and being reported even in Montevideo (Uruguay) the same day. On April 15th, the ash-fall was reported to have reached Rio de Janeiro, about 1,800 miles away. On Aug. 28th of the same year a hot north wind stirred up the ashes and dust, and there followed disastrous floods in Chubut Territory, similar to those which had occurred in 1889 after a volcanic ash-fall. The whole country passed through an unusually rainy winter (corresponding to our summer).

By interfering with the normal passage of solar radiations, as well as by furnishing nuclei for the deposit of moisture to

form fog, coal smoke, if present on a large enough scale (as in some parts of England), may exert an effect upon weather conditions. It is quite probable that a noticeable improvement could be made in the atmospheric conditions of London, if some way could be found to reduce materially the generation of nuclei from the enormous numbers of smoky domestic, factory, locomotive, and steamship fires. Public health would also be benefited, since the dust and fog interfere with beneficial ultraviolet solar rays. This is one reason why the "country" is healthier for children than the "city".

Carl Barus (Brown University; Smithsonian Contribution 1309 on "Atmospheric Nucleation," Washington, 1905) kept a continuous record of atmospheric nucleation for several years and found that the number of nuclei varied from about 2,000 to 100,000 per cubic centimeter. Such nuclei may be produced by violently agitating liquids, by heated bodies (red-hot metal or glass, a clear non-luminous Bunsen flame), by chemical activity (smokeless oxidation of phosphorous at about 13 deg.), by evaporation (*e.g.*, of sulphuric acid or naphthalene), by high potential (charged metal), and by certain kinds of radiation (ultra-violet light, X-rays, radioactivity). Barus says that the nuclei are at the outset simply dust particles small enough to float in the air, but larger than the order of molecular size, upon which water condenses. Most of them carry an electric charge. Atmospheric nucleation varied greatly from day to day and during the day, but was on the average greatest at the winter solstice (December 21) and least at the summer solstice (June 21), when less fuel is burned.

Following a tremendous fire at Campana, where oil tanks burned for a week, a "black rain" fell in Buenos Aires (Argentina), and the darkness of night did not lift all afternoon (Sept. 5th, 1934). The local Weather Bureau found that the rain was filled with microscopic particles of carbon and unburned petroleum. In the home, particles of unburned carbon, having high free surface affinities, tend to stick to walls and other surfaces where they are carried by air currents. Out of doors, such carbon particles make buildings grimy, and the sulphuric acid, usually also present, tends to corrode the stone, especially limestone.

To use a military term, molecules must be *deployed* before chemical reaction can take place rapidly and completely. Thus,

a log catches fire with difficulty and burns slowly; whereas the same log, if reduced to kindlings or shavings, would quickly flash into flame. Successful oil burners atomize or gasify the oil, and the Diesel internal combustion engine operates with atomized oil. In flames, the burning matter is largely in colloidal state, and when a combustible dust suspended in air approaches colloidal dimensions, its free surface becomes so great that it may burn with extreme rapidity if started by a static or frictional spark or the like (*explosive aerosols or dusts*). Great damage and loss of life have followed explosions of finely divided sugar, soap, starch, coal and the like.

Sodom and Gomorrah were probably destroyed by a colloidal cloud of petroleum ignited by local fires or lightning. Analogous phenomena are known in the Caucasus Mountains today.

The formation of mushroom-shaped clouds above volcanos in the course of violent eruptions as well as at times of relative quiescence, is due to the formation of a more or less stable aerosol, which forms a roughly circular blanket above the crater and is bellied upward in the center by the currents of hot vapors rising from the vent. The writer was fortunate in being able to witness the formation of a "mushroom cap" on Mt. Etna, Sicily, in 1933 (period of quiescence). On emergence the vapors appeared relatively clear, but owing to the low temperature at such altitude (nearly 11,000 feet), and the lack of breeze, they quickly condensed above the peak, forming a circular cloud that grew denser and darker as it grew older. From the bellying center the aerosol flowed downward towards the sides, and the outer edges were turned inward and under by air currents flowing toward the vent at the crater level. It seems reasonable to believe that the stability of the aerosol is mainly due to the charges borne by its particles, mutual repulsion inhibiting their coalescence. As the particles gradually aggregate, these electric charges would tend to migrate to their outer surfaces, giving rise to the high potential differences responsible for the terrifying displays of lightning which often accompany violent eruptions, while condensed water (generally acidulated) and aggregated solids fall as a muddy rain.

The electrical precipitation of colloidal and finely dispersed substances from air, smoke, furnace gases, etc., by the Cottrell process is too well known to be described in detail here. Un-

expected sources of profit are being found in the fumes compulsorily collected from cement kilns (potash) and from smelters (arsenic, selenium, etc.). Many dusts and mists (including sulphuric acid, which is a very good nucleator) that had defied ordinary bag-house methods are readily separated out by the high tension current. Sir Oliver Lodge even suggested that ships might thus clear their path of fog for some distance ahead.

Prof. W. D. Bancroft (Cornell University) and L. F. Warren demonstrated that electrified sand, scattered by an airplane, could cause the coagulation of fog and clouds, thus producing even a slight localized "rain."

One case where smoke is intentionally produced is in the use of "smudge pots," which are burned in orchards in the spring or early summer when indications are that the tender blossoms or fruit are about to be injured by frost. Besides smutting the fruit, the black smudge drifts about, blackening persons, clothing, and furnishings, and even leading to automobile and train collisions. One great lemon orchardist in California is said to have spent \$10,000 a night, employing 250 men, and using seven tank-cars of crude oil. This remedy is, of course, ineffective in very cold weather, but often serves to prevent what agriculturists term a light frost, which has for its precursors a still, clear atmosphere and a temperature approximating the freezing point. Frosts of this kind do not occur on cloudy or windy nights.

In the absence of smoke, the freezing process seems to proceed as follows: With falling temperature frost may deposit directly, or a dew-like deposit of water forms on leaves, buds, fruit and similar surfaces, and is congealed into ice crystals or "frost" when the slight heat liberated by the condensation radiates into the surrounding cold atmosphere; the freezing is facilitated by the evaporation of part of the deposited water. While the heat generated by the burning smudge oil is a large factor, the smoke liberated furnishes throughout the entire lower atmosphere innumerable nuclei upon which moisture deposits, with the liberation of some heat and the formation of a protective fog blanket that tends to check terrestrial radiation. The combination of all these factors is usually sufficient to ward off the threatened calamity.

These views are strengthened by the observations of Lieutenant B. H. Wyatt (Science, Sept. 21, 1923, p. 223) who, during

the recent total eclipse of the sun, took observations while flying in an airplane in a comparatively clear layer at an altitude of 13,000 ft. "During totality the recording thermometer at this altitude showed a rise of three and one-half degrees Fahrenheit instead of the anticipated drop period. The humidity fell from sixty-three to fifty-two per cent." This seems to indicate a liberation of heat upon the condensation of moisture, providing he did not enter a different stratum of air.

The author recently suggested that if the place and time of the formation of hail could be reasonably forecast, from meteorological observations and experience, at least a mitigation of the damage might be effected by burning nuclei-forming rubbish on a large scale to produce nuclei in the upper atmosphere, which would lead to formation of a larger number of *smaller* hailstones, whose weight and "whipping" and destructive power decreases as the cube of their diameters. A relatively small mass of matter can be made to produce an incredibly huge number of nuclei, and while the gigantic forces of nature cannot be denied or stifled, they might be thus *diverted* so as to diminish damage, which, especially in the West and Northwest runs into many millions annually in wheat alone.

## CHEMICAL WARFARE

The World War (1914-1919) resulted in an enormous development of the use of artificial smokes and fogs in military and naval offensive and defensive operations. While in the old days attacks or retreats had often been made under cover of natural fog or mist, now soldiers crept to the attack under the protection of a smoke barrage, and on sea destroyers laid down a smoke screen, or steamers sought, like the cuttlefish, to escape submarines in colloidal clouds of their own making. In the air natural clouds were lurking places for airplanes and dirigibles, and many air craft, especially Zeppelins, produced colloidal clouds in which they were lost to view.

The colloid-chemical aspects of chemical warfare may be epitomized as follows:

(1) *Offense*. Smokes or mists may be formed by the dispersion of irritant or otherwise harmful substances by bombs, shells, portable sprayers, etc., or such materials may be generated



and aggregate to colloidal dimensions, often on atmospheric or incidentally produced nuclei; *e.g.*, smoke candles.

(2) *Defense*. Gas masks are essential to filter out irritant or toxic smokes and dusts, and to adsorb, neutralize, or render innocuous toxic gases or vapors.

(3) *Signalling*. Organic dyes (*e.g.*, auramine, indigo, "para" reds) may be vaporized by the "*smothered*" combustion of lactose and potassium chlorate (otherwise a very dangerously explosive mixture), yielding colored clouds that may be used for signals, *e.g.*, in fireworks.

The main smoke producers used in the great war were phosphorus; sulphur trioxide (used as *oleum*, its solution in sulphuric acid); chlorosulphonic acid; tin, silicon, and titanium tetrachlorides, which are hydrolyzed by atmospheric moisture into their respective hydrated oxides and hydrochloric acid vapor; ammonium chloride. Smoke candles were made from mixtures of zinc, zinc oxide and chlorides of carbon (*e.g.*,  $\text{CCl}_4$ ,  $\text{C}_2\text{Cl}_6$ ).

The main irritant smoke producers were Lewisite ( $\beta$ -chlorvinylchlorarsine), diphenylchlorarsine (D.A.), and diphenylaminechlorarsine (D.M.). The finer they are dispersed, the more dangerous and lasting is the smoke. When first used, the subdivision was relatively coarse and produced violent sneezing, for even one part of D. M. in 10 million parts of air produces irritation. But finer dispersions were found to exert a serious toxic effect. There was a time of great anxiety until adequate defense against these dangerous colloidal dusts was discovered.

There are many examples of "chemical warfare" among animals. Spiders, snakes, wasps, bees, centipedes, are among those that give poisonous injections. The bombardier beetle (Order, *Carabidae*, Genus, *Brachinus*) ejects a fluid which volatilizes explosively, giving a puff of smoke and a distinct report. The vapor is acid and corrosive, and the smoke may completely hide the beetle. The chemical armament of the skunk backs up the dignity and deliberate assurance with which he moves.

The use of chemical warfare goes far back into history. In besieging Platatea, B. C. 429, the Spartans lighted huge pots of sulphur, pitch, and charcoal near the city's walls. The invention of "stink bombs" is credited to the Chinese, but they were also known in the Middle Ages. The Austrian chemist, Ulit Wulff von Snefftenberg, said in 1573: "It is a terrible thing. Christians

should not use it against Christians, but they may use it against the Turks and other unbelievers to harm them." Under cover of a cloud of smoke produced from damp straw, Gustavus Adolphus in 1632 crossed the Lech River near Augsburg, and defeated his unsuspecting enemy. Charles XII of Sweden used a similar device in 1699 to cross the Dvina River and defeat the Saxons.

The objections to chemical warfare are those which may be justly aimed at all warfare, but its novelty, effectiveness, and lack of adequate defense made it appear especially terrifying. Its cheapness, power, and mobility recommend it, despite treaties to the contrary. "At best, war is a brutal and unethical procedure, the only excuse for it being necessity, the tyrant's plea. The hope of the future is that all mankind may become so enlightened that the admirable qualities of courage, faithfulness, and sacrifice shown by men in war may be sublimated so as to win the less spectacular but more important battles against pain, unhappiness and disease." (J. Alexander in Alexander's "Colloid Chemistry," Vol. III, p. 239.)

## PERFUMES, ODOR AND TASTE

Without attempting to go into the question of what constitutes the sense of smell from a nervous or psychological standpoint, it may be said that the sensation of smell or odor is aroused only by the transmission of material particles which must be very small, since they pass readily through paper, textiles and the smallest crevices, and are held back only by airtight surfaces like glass or metal. The extremely minute quantities of many substances needed for their recognition by the sense of smell leads one to the view that their molecules may act as "modifiers" (see below) of the cellular catalysts within the specific cells in the nose, wherein resides the power to sense and distinguish odors. The effect is relatively transient, though some odors and stenchs seem to leave a more lasting impression on us, even after the source of the odor is removed.

Some gases have distinct odors, but from the fact that Barus ["The Structure of the Nucleus," Smithsonian Contribution 1373, Washington, 1903] was able to demonstrate the presence of colloidal nuclei in gasoline, benzol and carbon disulphide vapors, it is obvious that the presence of such particles is much more

common than has been believed. It is a question whether these nuclei arise from molecular association or from the condensation of vapor on smaller atmospheric nuclei. The persistency of naphthalene nuclei and their tendency to reach a fixed diameter led Barus to remark that "it is probable that the vapor pressure of naphthalene, however small, is the cause of this long maintenance of the supply of nuclei, and one may suspect that other bodies with strong odors and which show a tendency to slow sublimation will be found in like degree nuclei-producing."

Ambergris evidently owes its "body-producing" effect in perfumes to the formation by it of nuclei which have the power of strongly condensing the vapors of the ethereal oils, etc., which constitute the odoriferous ingredients of perfumes. Thus Barus found that paraffin nuclei, made by shaking a benzol solution of paraffin, disappeared with relative rapidity. This field offers an interesting vista of research, which may lead to a cheaper or superior substitute for ambergris, among other things.

In modern society, smell is a sense that is largely *tabu*, although throughout the whole animal kingdom it is of prime importance and utility. Wild animals are guided largely by it, and insects seem to be also. The highly developed sense of smell in dogs is widely utilized in hunting and trailing, *e.g.*, with "blood-hounds." Some scientists, experimenting with a single female moth which was confined in a cage in the middle of the city of Zurich, were astonished by large numbers of male moths which flew in their open window, although their laboratory was quite a distance from even the nearest park. On the author's farm there are two abandoned currant bushes, which are completely buried in a grove of trees and saplings; yet the currant worm moth visits them regularly, every year. The "tent-caterpillar" (fall web-worm) selects wild cherry and apple trees for laying its eggs. The fears and the favorites of most wild animals are determined by their sense of smell, to a great extent.

In primitive animals the cortex of the cerebrum (the *archipallium*) is mainly a center of correlation for olfactory impulses, which is the basis of the "higher" mental life in lower animals. With the higher animals, including man, the greatly developed *neopallium* portion of the cerebrum, whose functions are mainly visual and auditory, dominates; and in man the sense of smell is secondary. However, it is curious how many subconscious mem-

ories may be awakened by an odor, especially by odors associated with happenings impressed on the brain by sharp or repeated nervous impulses. From this point of view, memory appears to be a form of hysteresis (see p. 149) impressed on the brain col-loids by electrical nerve currents.

The path from the olfactory organs to the brain is extremely short, shorter even than those from the eye or ear; and the ol-factory center in the brain is very close to the pituitary gland (hypophysis), the "director of the endocrine orchestra." Many things which we believe we taste are really smelled, as may be readily proven by holding the nose while tasting such substances as chocolate, vanilla, etc.

It is not known how specific molecules, reaching the olfactory organs, arouse in consciousness awareness of specific "smells". One possible step in the process may be specific modification (see p. 375) of cellular catalysts, whereby most minute quantities of the incoming substance could effect a relatively large amount of intracellular change, of a nature corresponding to the exciting molecules. The sense of taste may be controlled by a similar mechanism. C. A. Elsberg, Irwin Levy and E. D. Brewer (*Science* 1936, 83, 211), experimenting on normal persons and others with brain tumors, found that olfactory fatigue is not due to refractory state of the olfactory receptors or of the olfactory bulbs and tracts, but results from "an abeyance of function in the receptive and memory centers for smell in the brain itself."

H. C. Moir (*Chemistry and Industry*, 1936, 55, 146) tested the ability of 60 persons, selected at random, to distinguish four flavors: Orange, lemon, lime, and vanilla. The results showed only five with records of over 75%, one being perfect. Forty-eight had less than 50%. Vanilla was identified as black currant, lime, apricot, greengage, damson, lemon, pineapple, orange, tangerine, almond, red currant, strawberry. Before attempting to pass judgment on flavors in matters which concern persons other than himself, a chemist should be sure that he himself has the requisite discriminative capacity. Experience is also needed to decide, for commercial purposes, *what the average person* will be apt to decide as to flavor.

Recently, scientific support has been found for the ancient maxim: "De gustibus non disputandum est." The taste of phenylthiocarbamide depends on who is tasting it. About 30%

of all those tested found it to be tasteless; but most people describe the taste as "bitter," while others find it "sweet," "sour," "salty," etc. Blakeslee and Fox found that inability to taste this substance is inherited, apparently as a Mendelian recessive character (see p. 342). Dr. Stephen Miall (Chemistry and Industry, 1932, 51, 769) states that only a limited number of persons can taste sodium benzoate, and that wide differences exist in ability to detect or recognize such odors as verbenal. He states: "It is well known among chemists that the possession of a delicate palate for fine wines is an inherited character, though there is also evidence that it may be acquired." Perhaps it would be better to say "cultivated," because it might not be possible to go beyond inherited barriers.

The *relativity of sense phenomena* thus comes sharply to our attention. Our very senses, upon which we rely for information as to the external world, differ with different persons; and these differences, being in part at least of genetic nature, must involve differences at ultramicroscopic levels and be ultimately explicable in chemical and physicochemical terms. (See J. Alexander, *Scientia*, October, 1933). In some cases, these personal differences may explain the deviations sometimes found among witnesses, as to just "what happened." It has been said that the eye sees in it only what the brain gives it the power to see.

While some odors are due to molecularly dispersed particles, in many cases we have to deal with colloidal particles; and it will be of interest to investigate the permeability of septa to smells. The odors of many substances are due to impurities. Thus absolutely pure sulfuretted hydrogen, carbon disulfide and phenol are said to be without marked odor, as are also pure indol and skatol.

Foods, tobacco, and the like may absorb or adsorb fumes, vapors, or odors diffusing from various sources, and thus acquire a *taint*. This happens in household refrigerators, but is much more apt to happen in the holds of ships where the taint may arise from leaking fuel oil, contaminated dunnage, disinfectants, or other cargo. For example, butter and eggs are often contaminated by oranges, cabbage, etc., and tobacco may be tainted by goat skins, etc. Although the quantities of tainting substance may be minute, its precise nature unknown, and the effect psychological, the loss in commercial value may be great. Good

stowage of cargo demands proper isolation of cargo susceptible to taint, and in the icebox it is wisest to keep both "smelly" and sensitive foods in closed containers. Fats readily absorb odors, and are, in fact, used for this purpose in the "enfleurage" process of obtaining flower perfumes.

## GEOLOGY

Coming back to solid earth, let us consider the ordinary properties and behavior of the earth's solid constituents. These depend more upon their state of physical dispersion than upon their chemical constitution, as may be seen by considering Atterberg's classification of minerals according to the size of their fragments:

TABLE XVIII

	Diameter			
Boulders.....	2	m.	to 20	cm.
Pebbles.....	20	cm.	to 2	cm.
Gravel.....	2	cm.	to 2	mm.
Sand.....	2	mm.	to 0.2	mm.
Earth.....	0.2	mm.	to 0.02	mm.
Loam.....	0.02	mm.	to 0.002	mm.
Clay.....		smaller than	0.002	mm.

The finer particles are more readily blown about by the wind and carried and deposited into sedimentary beds by water; they are more soluble and are more easily leached and decomposed by "weathering." In mass the finer particles are less permeable to water, but possess a much higher capillarity and water-holding capacity, besides a powerful fixing or decomposing action on diffusing substances. Thus if dilute potassium sulphate solution is percolated through a column of fine sand, free sulphuric acid is found in the percolate.

A few instances may be mentioned to show the tremendous masses of finely divided matter carried great distances by the winds. Hellman and Meimardus report that about March 8-10, 1901, a cyclonic storm central over Tunis sucked up dusts raised from the deserts of southern Algeria to such high levels, that about one-third of the 1,800,000 tons that fell in Europe, was deposited north of the Alps. Great quantities fell into the Mediterranean Sea and 150,000,000 tons was estimated to have fallen on the African Coast. E. R. Miller and A. W. Winchell reported

on a storm of dust-discolored snow over an area of 100,000 square miles (from Dubuque, Iowa, to Chelsea, Vermont) and estimated that the million or so tons deposited must have come from the arid Southwest (Arizona, New Mexico) and must have been carried over 1,000 miles at high altitudes *before* it began to fall.

Dr. Roy Chapman Andrews (American Museum of Natural History, N. Y.) has reported on the tremendous erosive effects of wind and water on the soils of Manchuria and western China, and also on the huge dust, sand, and gravel storms in the Gobi Desert. In Peiping during dust storms, lamps are kept lit all day, and marines stationed there know an ailment called "Peiping throat," caused by breathing the begrimed air. A film of brown dust covers the page of your book before you can turn it, and dust clogs your fountain pen before you can finish writing a letter. Slight in comparison was the dust storm which swept over New York on May 12th, 1934, although no greater one is remembered there. It is estimated that 300,000,000 tons of soil were lifted from the drought-parched Western States by a strong north-west wind and sprinkled over half the nation. See "Science," May 25th, 1934.)

The terrible dust storms which occurred recently, especially in the spring of 1935, followed a severe and prolonged drought in the middle and southwestern parts of the United States (see, *e.g.*, N. Y. Times of April 12th, 1935). Wind-blown dust was carried as far as the Atlantic States, besides being otherwise widely distributed. It caused much loss of crops and animals, and some localities reported "dust pneumonia."

Prof. Y. Wada states that on March 4, 1915, a "sand mist" consisting of dust from the interior of China moistened by accumulated water, deposited a one-fourth inch layer of dust at Etchu Province, Japan.

Between January and April it is common to meet at sea, west of Africa, falls of dust from the Sahara, which probably accounts for the legend of a "Sea of Darkness" lying between the Canaries and Cape Verde Islands. In 1898 the S. S. "Roslin Castle" sailed through about 900 miles of dense haze in that region, and S. S. "Tintagel Castle" was detained thirty hours by it.

The eruption of Mount Pelée, which destroyed Martinique and 30,000 of its people, cast exploded ash so high that for several days the fall continued. The S. S. "Roddam," lying

nearby, received a heavy coat. Scientific men arriving a week later found the air full of fine ash, some of which was still afloat then; ten weeks later another explosion scattered white ash over the whole West Indies.

Fine deflocculated clay is carried thousands of miles by rivers, and when finally coagulated by the salts of the ocean forms new land. Geological evidence shows that this process has added about a thousand miles to the length of the Mississippi River, and owing to the enormous areas under cultivation (which permit more soil to be carried off) it is going on perhaps faster than ever. Its results may be seen at the mouth or delta of every large river—the Nile, Ganges, Hwang-Ho, Amazon, Euphrates. The great weight thus accumulated at certain weak places in the earth's crust may cause slip along lines of geological fault. The recent (1923) destructive earthquake in Japan is believed to have had such an origin.

The presence of fine particles in water produces many beautiful effects in nature. This is marked in limestone glaciated regions, and seems to be due to the fact that the cold glacier water dissolves quite a bit of atmospheric carbonic acid and takes up some limestone in solution (as bicarbonate), the mineral being afterwards thrown out in colloidal state as the temperature of the water rises. This appears to be the case at Lake Louise in the Canadian Rockies, for the coarser material brought down from the Victoria Glacier is deposited at the head of the Lake. Variations in color of the water, as in Emerald Lake, "Blue River," etc., involve differences in depth and in light effects, and probably also in colloidal protection and in physico-chemical conditions leading to variation in acidity and rate of temperature change, which would affect the particle size of the precipitated calcium carbonate. Analogous effects exist along the "Blue Mediterranean," and in the famous "Blue Grotto" of Capri, also in Lake Geneva and in Swiss glacier streams.

Fine particles generally have been deposited in huge thick beds by glacial and other prehistoric waters, which have mostly graded them according to size. Such deposits, when cemented by pressure, dehydration or igneous or metamorphic action, became slate, shale, sandstone, etc. When they enclosed pebbles, the result was "pudding stone," and they frequently served as a



matrix for fossils and as a means to preserve fossil footprints, ripple marks, and even rain splashes.

Baron Gerard De Geer, after studying the laminated clay deposits of Sweden, and comparing them with other similar deposits in northern Europe, was able to estimate that it took about 13,500 years for the continental glacier to retreat across Sweden. Following the regular cycle of the seasons, the intermittently melting ice poured silt-laden waters into the fresh water 'lakes' impounded in front of the glaciers. With the coming of autumn, as melting waned and the amount and turbulence of the glacial streams fell off, the quantity and coarseness of the sediment diminished, a layer of fine, fat clay marking the close of the year's deposit; after which winter froze everything up until the following spring. "In southern and central Sweden 5,000 years have been established, with an almost negligible limit of possible error, and in northern Sweden 8,500 years with a possible error of one or two centuries" (Prof. James W. Kemp (Columbia University), "Natural History," Vol. 22, Jan.-Feb., 1921).

"Various interesting corollaries follow. For instance, a deposit of prehistoric flint instruments has been found on a delta in Sweden, whose relations with known laminated clays can be made out, giving a pretty accurate clue to the number of years ago that primitive users of flint followed the retreating ice into Sweden. Again, the continental glacier extinguished plant life, and, on its retreat, gradually the vegetation followed it northward. The actual number of years can now be quite closely made out, and the time required to change inhospitable sands, gravels, and clays to soils capable of supporting the present plants and trees\* can be determined. A chronology is afforded for the distribution not alone of plants, but of animals as well."

Eozoon, long thought to represent the fossilized remains of primeval plant life, is probably nothing but an instance of rhythmic precipitation (Liesegang's rings), which often occur when precipitates are formed by diffusion into colloidal gels.

### MINERALOGY

Agates, onyx and dendrites are types of minerals formed by rhythmic precipitation (Liesegang's rings), and ore bodies may

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\* See p. 197 on soil erosion. The laminated clay deposits are termed *varves*.

be deposited by similar segregating action. Some minerals are themselves colloidal gels (*e.g.*, opal, flint, bauxite) or result from other minerals by weathering with subsequent gel formation (*e.g.*, kaolin from kaolinite, serpentine from diabase). V. Lenher (University of Wisconsin) has recently shown that mere trituration is sufficient to bring silica into colloidal solution, and it seems that many quartz minerals have been deposited, in part at least, from colloidal solution. The same applied to stalactites and stalagmites, for with a fluctuating carbon dioxide content, especially in the presence of protectors like humus, some colloidal calcium carbonate will be formed.

At Mammoth Hot Springs (Yellowstone Park, U. S. A.) the calcium carbonate brought up by the rising waters is quickly thrown out as the water cools and the contained carbon dioxide escapes. In addition to these factors making for fine subdivision, algae growing on the faces of the "terraces" furnish a protective colloidal slime. As a consequence, the freshly deposited mineral is cryptocrystalline. But on ascending the high hill and examining older and older deposits (the oldest estimated at 25,000 to 30,000 years old), a progressive increase in crystallinity is evident; near the top the deposit is coarsely crystalline, the forces of crystallization slowly asserting themselves. It is not often that one can read the results of an experiment after so many years.

## GEMS

Many gem stones owe their beautiful colors to impurities colloiddally dispersed in them—the emerald to chromium, the ruby to iron, the amethyst probably to manganese, the topaz to iron, etc. The varying shades of diamonds seem to be due to similar causes. Opals are gels with interior reflecting planes. The shade and even the color of many gems can be changed by subjecting them to the action of X-rays or radium, which apparently act by bringing the dispersed particles into a different state of aggregation, usually coarser.

Pearl scales, when examined in the dark field, show the inhibited crystallization characteristic of crystals formed in the presence of a protective colloid, which here is the slime or mucin of the mollusc. There is no reason to doubt that colloid research

will lead to the synthetic production of mother-of-pearl, and perhaps even of substitutes for the real pearl itself.

Since the writing of the above there appeared in "Chimie et Industrie," Vol. 8, p. 782 (1922), a paper by Clément and Rivière, describing the production of artificial mother-of-pearl, by precipitating calcium carbonate under chosen conditions in a colloidal medium. (See also Alexander's "Colloid Chemistry, Theoretical and Applied," Vol. III.) Imitation pearls have been made by coating transparent hollow glass beads on the inside with a lacquer containing finely comminuted scales (pearl essence) of a certain silvery fish, and then filling in with wax. Recently, colloiddally precipitated calomel has been used in place of fish scales.

The author found, on (dark-field) ultramicroscopic examination of opal, the extremely fine "cracks" in *opal* responsible for its beautiful play of colors. These are referred to by l'Abbé Haüy in his treatise on physics (1803), and the phenomenon is there mentioned as analogous to the colors of Newton's rings.

Besides clear gem *diamonds*, three classes of industrial diamonds are known: (1) *Boarts*, more or less transparent crystals, of bright appearance, occurring in varied shapes; (2) *Carbons* (carbonado, black Brazilian diamonds), sometimes called amorphous diamonds, but really composed of masses of very tiny crystals, with a fracture resembling that of fine steel and an intense hardness, greatly exceeding that of boarts; (3) *Ballas*, ball-like aggregations of small, well-formed crystals concentrically grouped around a nucleus. Having no cleavage planes they are also extremely hard, and rather tougher than carbons, which they are used to test. When a ballas and a carbon are rubbed together, a white mark indicates that the carbon is harder, while a dark-brown mark indicates that the ballas is harder. Where the stones are equally hard, no mark results.

Through the kindness of Prof. George L. Clark (University of Illinois), I was able to secure X-ray spectrograms of a ballas, a very hard carbon, and a softer carbon. The results indicated that the ballas was composed of many small crystals, the softer carbon of smaller and more numerous crystals, while in the harder carbon many of the crystals approximated colloidal dimensions, the rings of the X-ray spectrogram being continuous, with many small spots. *The space lattice throughout is that of diamond*, the variations in hardness being primarily consequent

upon variation in particle size and structure of the aggregates. Therefore we must reconsider the statement in J. W. Mellor's monumental book ("A Comprehensive Treatise on Inorganic and Theoretical Chemistry," 1924, Vol. V, p. 720) that "boart and carbonado are usually regarded as forms intermediate between diamond and graphite." (See J. Alexander, "Science," 1931, 63, 185-6.)

## CHAPTER X

### PRACTICAL APPLICATIONS (*Continued*)

#### AGRICULTURE

ALTHOUGH from time immemorial farmers have classified soils on the basis of their physical and physiological character as "light" or "heavy," "rich" or "poor," "productive" or "unproductive," etc., it is only within comparatively recent years that chemists have begun to realize the full importance of the rôle played by the colloids, especially the organic colloids of the soil.

The constituents of the soil fall into three classes:

1. Mineral fragments, consisting mainly of silica and silicates, resulting from the disintegration of rocks by weather, water, heat, freezing, etc.
2. Organic material, including bacteria, and that mixture of plant and animal debris known as humus.
3. Soil solution, which is water with its various solutes.

The fact that colloids occur in all three of these classes should serve to reconcile the older hypothesis that the colloidal behavior of clay is due to fine particles, with the more recent view that it is due to a jelly-like "ultra-clay" which surrounds the particles. Both conditions exist and exert an influence. The "ultra-clay" evidently consists largely of colloidal humus, for the smallest particles, with which it exhibits its main effect, have the largest percentage of organic matter.

Among the natural agencies tending to increase the size of the minute soil particles may be mentioned heat with its drying or evaporative effect, freezing, and the coagulating or flocculating action of soluble inorganic salts and some organic substances present in the soil. On the other hand, included in that little known class of substances vaguely described as "humus," there are numerous organic substances derived from the bacterial, plant, or animal débris, or exuded by the roots of plants, which act as protective colloids (*Schutzkolloide*) and tend to produce and maintain the hydrosol, or deflocculated condition. (See P. Ehren-

berg, "Die Kollide des Ackerbodens," *Zeits. angew. Chem.* 1908, 41, 2122.) In an excellent paper on the mechanics of soil moisture, L. J. Briggs (U. S. Dept. of Agric., Bureau of Soils, Bull. No. 10, 1897) pointed out that very small quantities of certain organic substances, such as are continually being produced in the soil by the decay of organic matter, greatly decrease the surface tension of solutions, thus counteracting to a large extent the effects of the surface application of soluble salts which would tend to draw moisture to the surface by increasing the surface tension of the capillary water of soils. It is well known, however, that an excess of salts will ruin a soil physically, as is evident after flooding by sea water or the excessive application of chemical fertilizers. Of interest in this connection is the recent work of the Bureau of Soils, U. S. Department of Agriculture, carried out by Cameron, Schreiner, Livingston, Gile, Davis, and their co-workers. Thus plants grown in the unproductive Takoma soil were greatly benefited by green manure, oak leaves, tannin and pyrogallol. The injurious effects of quinone and some other organic substances may be due to their ability to precipitate or flocculate the protective colloids of the soil; for as Lumière and Seyewetz have shown (*Bull. Soc. Chim.*, 1907, 4, 428-431; *J. S. C. I.*, 1907, 703), quinone renders gelatin insoluble.

The fact observed by Fickenday (*J. Landw.*, 1906, 54, 343) that more alkali is required to flocculate natural clay soils than kaolin suspensions, he attributes to the protective action of the humus present (see Keppeler and Spangenberg, *J. Landw.*, 1907, 55, 299).

A. S. Cushman [*U. S. Dept. Agri., Bureau of Plant Industry, Bull. No. 104*] showed that fine grinding of feldspar greatly increased the amount of potash available under the action of water. A coarse powder whose free surface was 43 sq. cm. per cc. yielded only 0.013 per cent., whereas a fine powder with a free surface of 501,468 sq. cm. per cc. yielded 0.873 per cent. of potash and soda, an increase of 6,700 per cent. Even then these fine particles averaged about 0.1 micron in diameter, which is about the upper limit of colloidal dimensions. In the soil they undergo further disintegration whereby still more of their potash becomes available. The availability of phosphate rock is greatly increased by fine grinding.

Many factors oppose the agriculturally undesirable tendency of humus to deflocculate clay, which would permit the rain to wash it away: (1) In suitable concentrations humus and clay act as oppositely charged colloids, and mutually precipitate each other; (2) the lime present in most soils forms with the humus a gel of the insoluble calcium humate, which sticks the soil particles together. Generally an excess alkalinity due to soda produces the evil effects found in the heavy, sticky alkali soils.

When all these factors are properly balanced, the soil is in good *tilth*, which Sir E. J. Russell defines as that "nice crumbly condition suitable for a seed bed." This permits proper drainage and circulation of air essential to bacterial activity and plant growth. Humus acts as a stabilizer. It makes the soil less sensitive to the ruinous coagulating effects of an excess of salts. Thus 15 to 20 per cent. of humus will almost obliterate the difference between a clay soil and a sandy soil. "Humic acid" is a mixture of allied substances rather than a definite chemical entity. Its calcium "salt" exercises a buffer action by combining with injurious acids and liberating the harmless, insoluble humic acid.

Many important properties of a soil, such as permeability, capillarity, absorption, moisture content, etc., are dependent not so much upon the chemical composition as upon the sizes of its constituent particles. In coarse sand, for example, the amount of water is greatest at the bottom and smallest at the top, whereas in fine clay the distribution is much more uniform. Clay consists of particles 0.002 mm. (2 microns) in diameter and smaller. Over about 18 per cent. clay gives a heavy soil, while under about 4 per cent. means a sandy soil of low water-retaining capacity.\* The effect of lime is so marked that a dressing of calcium carbonate will make an 18 per cent. clay soil act like a 12 to 14 per cent. soil, partly through the formation of calcium humate gel, which cements the finer particles into the desirable crumbly condition.

This also makes ploughing much easier; thus in the 1921-22 report of the Rothamsted Experiment Station it is stated that chalking heavy soil may reduce the power needed for ploughing by as much as 15 per cent.

Apart from the activity of bacteria, earth-worms and the like, the movement of substances in the soil is effected by diffusion

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\* The application of colloidal clay or bentonite might be useful in such cases.

and seepage of soil water. The forces acting may be divided into three groups, although, of course, there is no sharp line of demarcation between them: (1) Molecular forces of the order of 1,000 atmospheres; (2) capillary forces of the order of 3 to 4 atmospheres; (3) gravity. This corresponds roughly to the classification of soil water by Bouyoucos, as follows:

Gravitational water—"super-available."  
 Free water—very available.  
 Unfree water { capillary-absorbed—slightly available.  
                   { combined { solid solution } —unavailable.  
                                   { hydration }

The leaf system of plants is continually evaporating moisture, and the resulting hydration and osmotic "pull" is sufficient to raise a column of water even to the top of the tallest sequoia tree. It is registered as a root pull of about 7 to 8 atmospheres. The water evaporated by plants is continually replaced by rain, but in dry weather there results a struggle for water between the plant and the soil. The percentage of water left in the soil when the plant can no longer protect itself against desiccation by taking up soil moisture is called the *wilting coefficient*. Its value varies with different plants, and the great influence of particle size of the soil may be seen from the following table of the shrinking coefficient of Kubanka wheat (after Briggs & Shantz):

Soil	Wilting coefficient
Fine sand.....	2.59
Fine sandy loam.....	9.66
Clay loam.....	16.3

An important factor in the struggle between the "root pull" of the plant and the "back pull" of the soil is the speed with which water can diffuse toward the roots. Cultivation of the soil above the roots exposes a greater soil surface to the air, and the resulting increased evaporation there causes increased upward and side-wise diffusion streams, which not only supply water to the roots at increased speed, but also carry the necessary plant food. As Bechhold observed (*Kolloid-Zeit.* 27, 29, 1920), soluble salts follow diffusion streams. Thus if a piece of plaster of Paris be dipped in sulphate of copper solution and then dried, the copper



will be found almost quantitatively in the exterior layers. W. Kraus (Kolloid-Zeit. 28, 161, 1921) showed that this "capillary phenomenon" of salt concentration is due to evaporation at the exposed surfaces. The plant is therefore enabled to make its necessary growth with less water, and as this growth generally is greatest in the wet season, *cultivation* or *tillage* by losing some water may actually enable the plant to enter the dry season with a reserve store of soil water in the soil, which in turn is made more rapidly available in the dry season by further cultivation. (J. Alexander, Science 1921). Cultivation also kills off competing weeds and aids soil bacteria which produce plant food in available form. It also improves aeration of the soil.

Contrary to popular idea, colloids do diffuse, albeit more slowly than substances molecularly dispersed, so that the roots may absorb soil colloids which diffuse toward them. While, of course, chemical reactions may go on in the soil, ionizable or hydrolyzable salts are apt to be split up and their fractions segregated by the action of selective adsorption and differential diffusion, giving results that cannot be simulated by simple aqueous solutions. Changes in effective reaction (hydrogen ion concentration) and other conditions affect the state of the soil colloids, and as their active free surface varies, they may hold or release adsorbed substances. Protectors also exert their influence.

In very permeable or sandy soils, especially if deficient in lime which holds the humus as a gel, the alumina, iron and humus are apt to assume the sol form and be washed down by the rain to a lower stratum, where, by desiccation or electrolyte precipitation, they gradually form an insoluble rock-like layer known as a *pan*. Such a pan acts as an impermeable septum, shutting off the soil beneath from air and water, preventing diffusion between it and the top soil, and often causing swampy conditions.

The formation and past history of a soil have much to do with determining its properties, as may be seen from the following remarks on loess soils, kindly given me by Prof. Frederick K. Morris (Mass. Inst. of Technology).

Loess is a fine dust which has been carried by wind. It may be dropped when the wind slackens, or it may be washed out of the air by rain and held in place by vegetation. The true wind-borne loess is commonly associated with finely bedded water-borne silts, with which it should not be confused.

Loess is obtained by the wind from any widely exposed area of fine unconsolidated sediment which has no vegetation cover. The outwash aprons issuing from glaciers; the floodplains and deltas of summer-withered rivers; the badlands and playa-floors of deserts; the dry bottoms of shrinking lakes; areas of residuary soil on which the vegetation has been killed, especially through change of climate; areas exposed by ploughing in regions of light rainfall, are the typical sources of loess. Loess is therefore especially abundant in basin-lands adjoining deserts, along the margins of formerly glaciated regions, and where large lakes extended during Pleistocene time. The principal loess regions are: China north of the Yangtze river; Siberia north of the Khangai and Sayan slopes; southern Russia; Hungary; northern Germany; and in the United States, the central and northern Prairie Plains, parts of the Columbia and Snake River Plateau, and parts of the Great Basin and the Southwest Basin states.

The thickness of loess ranges from one to 300 feet, averaging 20 to 100 feet. It is massive, and locally shows a faint color-banding without bedding planes; locally grading into water-laid, stratified silts and gravels which are not true loess. The grains are angular and vary in size as shown in the following table:

Sample I			Sample II			
Fine sand.....	0.13	mm.	1.59%	0.10	mm.	1%
Very fine sand.....	0.065		27.44	0.063		25
Silt.....	0.033		50.97	0.030		54
Clay.....	0.0035		20.00	0.0004		20

The grains are well interlocked, indicating a slow rate of accumulation; and locally an incipient cementation by carbonate cement has developed. Vertical tubules, which are attributed to the roots and stems of the plants which originally entrapped the dust, traverse the deposits; but the vertical cleavage of loess is only partly due to these holes; it is chiefly a jointing phenomenon, due to tension in the mass. Loess is characteristically rich in concretions, which form in vertical positions due to precipitations of carbonates, chiefly of calcium, with less of  $MgCO_3$  and  $FeCO_3$ , and still less of  $MnCO_3$  and carbonates of alkali metals. The precipitates enclose the grains of loess, and so represent not only a filling of the vertical tubules, but a partial cementation of the loess. The irregular, knobby, vertical concretions have been

called "loessmännlein" or "loesspüppchen." In some loess deposits they are quite absent. Porosity has been determined by Lowdermilk \* as 47.8% (Barbour, loc. cit., page 462). Water travels much more freely in a vertical than in a horizontal direction in loess, because of the vertical tubules and vertical joints. Horizontally the only movement is through the very small and tortuous pores. The loess soils absorb water readily, and hold it. They are therefore rich in ground-water solutions. Being characteristically upland deposits, they are rarely in a position suitable for irrigation, and their high capacity for absorbing water renders irrigation unprofitable even where it is topographically possible. Loess soils are characteristically suitable for dry-farming and deep ploughing.†

#### PRINCIPLES UNDERLYING THE GENESIS AND CLASSIFICATION OF SOIL

*Soil colloids* ("the protoplasm of the soil") comprise an *inorganic* portion mainly alumino-silicates derived from the weathering of silicates, particularly the feldspathic minerals, and an *organic* portion composed of modified plant and animal remains and debris, *e.g.*, lignin, dead bacteria, moulds, animals, etc. The soil colloids behave somewhat as zeolites, taking up by base-exchange the various cations or bases in a manner depending on the concentrations which happen to be operative. The main cations are hydrogen, calcium, potassium, sodium and magnesium, and the properties of the soil-colloids containing various quantities of cations differ enormously.

The hydrogen-colloid is acid, and in the absence of flocculating electrolytes tends to form a colloidal dispersion. The sodium-colloid is very alkaline and most dispersible of all. The calcium-colloid is faintly alkaline and tends to maintain a flocculated state. The sodium-colloid, and under certain conditions the hydrogen-colloid, are leached from the surface (whereas the less easily dispersed calcium-colloid remains), and may later be flocculated by salts or differential diffusion or filtration in a lower soil layer or

\* From *China Journ. of Science and Arts*, Vol. III, p. 462; paper by C. B. Barbour (1925).

† See also Bryan, Kirk, "The Palouse Soil Problem," with an account of elephant remains in wind-borne soil on the Columbia Plateau of Washington, U. S. Geol. Survey Bulletin 790-B.

horizon, termed the "B" horizon. In the case of the hydrogen-colloid especially, the action of protective colloids is also a factor to be considered here. The lower horizon may thus accumulate a large percentage of clay, which, in turn, may be compacted into a "pan" or even a kind of sandstone.

*The Function of Water in Soil Formation.* Since the leaching above referred to requires water, the water-supply of the soil (rainfall, flooding, irrigation) is naturally determinative, and based upon the nature of the environmental conditions, there are recognized three main types of soil formation—*calcification*, *podzolization* and *laterization*.

*Calcification* takes place when the rainfall is insufficient to wash out the alkaline earth carbonates which are produced by the hydrolysis of silicate minerals and which accumulate in a horizon (or layer) at the bottom of the *soil profile* (downward cross section). The main vegetation consists of grasses and grass-like plants, which feed heavily on bases, especially calcium; bacteria are the principal organisms, and their remains are relatively insoluble. The calcium accumulates and maintains a flocculated condition of the colloids, conserving in the surface layer the organic matter. The following groups of soils produced under calcification are recognized:

1. *Chernozem* (from the Russian word for "black soil"). This is high in organic matter, and has a nut-like structure.
2. *Chestnut Soil*. Dark brown in color, with less organic matter than Chernozem, and a prismatic structure.
3. *Brown Soil*. Brown in color; prismatic structure. Less organic matter.
4. *Sierozem* (from the Russian, meaning "grey soil"). Low in organic matter.
5. *Desert Soils*
6. *Prairie Soils*
7. *Rendzinas* (Intrazonal)

The great wheat lands of America and Russia are Chernozems and Brown soils.

*Podzolization* results where the amount of moisture reaching the soil is sufficient to remove rather completely the salts of the alkalis and the alkaline earths. Forests constitute the main vegetation, and they do not accumulate bases to as great an extent

as the grasses. Fungi are the main organisms, the tannins from the trees exerting a toxic action on bacteria. Conifers (pine, spruce, hemlock) take up less bases, and shed their leaves more slowly than do the deciduous trees (*e.g.*, maple, elm, oak, poplar, birch), thus yielding less organic and mineral matter to the surface soil. There being insufficient bases to neutralize the carbonic acid brought down by the rain and other organic acids formed, the base exchange colloids become acid, and are leached down into the lower levels of the soil profile. Iron, reduced at the surface, is dissolved by organic acids, migrates downward, and is precipitated at lower levels under the influence of differential filtration and changing pH. (See p. 114.) In the case of the Podzol the hydrogen-colloids are partly broken down before translocation to the B horizon. Podzols have been largely stripped of bases and of colloids in the upper horizons. At the surface silica mainly remains, underlain by iron and alumina. While Podzols support naturally adapted vegetation, most plants cultivated for human food will not do well on them.

Just south of the Podzols are the Gray-Brown Podzolic Soils on which our Western civilization is largely developed. The temperatures are higher and the forests, mainly of deciduous trees, shed each year a relatively large amount of organic matter, and also return to the soil more bases than do the conifers. Podzolization is less marked, and these soils, though less fertile for most crops than Chernozems, surpass Podzols.

*Laterization* is characteristic of tropical and semi-tropical climates, with high temperatures and abundant water supply. Weathering of minerals is rapid, and vegetation grows and decomposes quickly, bringing large amounts of bases to the immediate surface, solubilizing the silica, and leaving mainly iron, alumina, and resistant silica (quartz). The content of bases becomes less and after they are finally washed out, podzolization supervenes.

*Salinization* yields *Solonchak* (saline soil), structureless, mildly alkaline, with flocculated colloids. If monovalent cations are present and drainage good, *solonization* supervenes, yielding *Solonetz* (black pillared alkali soil), highly alkaline, hard, prismatic in structure, with dispersible colloids. On continued leaching, *solodization* leads to the formation of *Soloth*, whitish, plate-

like, and acid near the surface, under which is a darker "B" horizon.

The sketches (Fig. 15) show profiles 56 inches deep, representing four of the great soil groups in equilibrium with different biological complexes and developed from the same parent material.\* The expression "biological complex" is used advisedly, because animals (including man) are of great importance in these matters. Darwin tells of a conifer browsed down by cattle for decades, and mentions that cats aid red clover because they prey on mice which plunder the nests of the bumble-bees which fertilize the clover flowers. When Itasca Park (Minnesota) became a refuge for "wild life," wolves were killed off—whereupon beaver and deer, increasing enormously, destroyed so many aspen trees and pines, that the normal soil development was upset. The destruction of forests by man, the removal of protective grasses, etc., and ploughing and cultivation, have produced a problem of *soil erosion* on certain soils which have been used for purposes or in ways to which they are naturally unsuited.

More than 17,000,000 acres of land in the United States have been rendered uncultivable or nearly so, by erosion induced through incorrect land-use, and the annual loss of plant nutrients by erosion is estimated at about 125,000,000 pounds with a value of \$200,000,000, to say nothing of the further expense necessitated for the removal of deposited silt from river channels and harbors. The pernicious practice of leasing land without incidental provision for its maintenance, and the feeling that "worn-out" land can be abandoned for new fields, will disappear as the more complete development of the country enforces the necessity of more careful and intensive agriculture. The gullies, bitten into the land by flood waters, are being fought by terracing, a practice used by the Incas and common in the Far East. Many years are required to develop fertile soil, and its conservation as a national asset is imperative. The whole matter of soil conservation is predicated upon knowledge of individual soil types and their capabilities for use.

\* This Figure is taken from a paper by Dr. Charles E. Kellogg, Bureau of Chemistry and Soils, U. S. Department of Agriculture, and this brief outline of the now important science of pedology (the science of soils) has as an additional basis further information kindly sent me by Dr. Kellogg.

# GENERAL SCHEME OF SOIL CLASSIFICATION

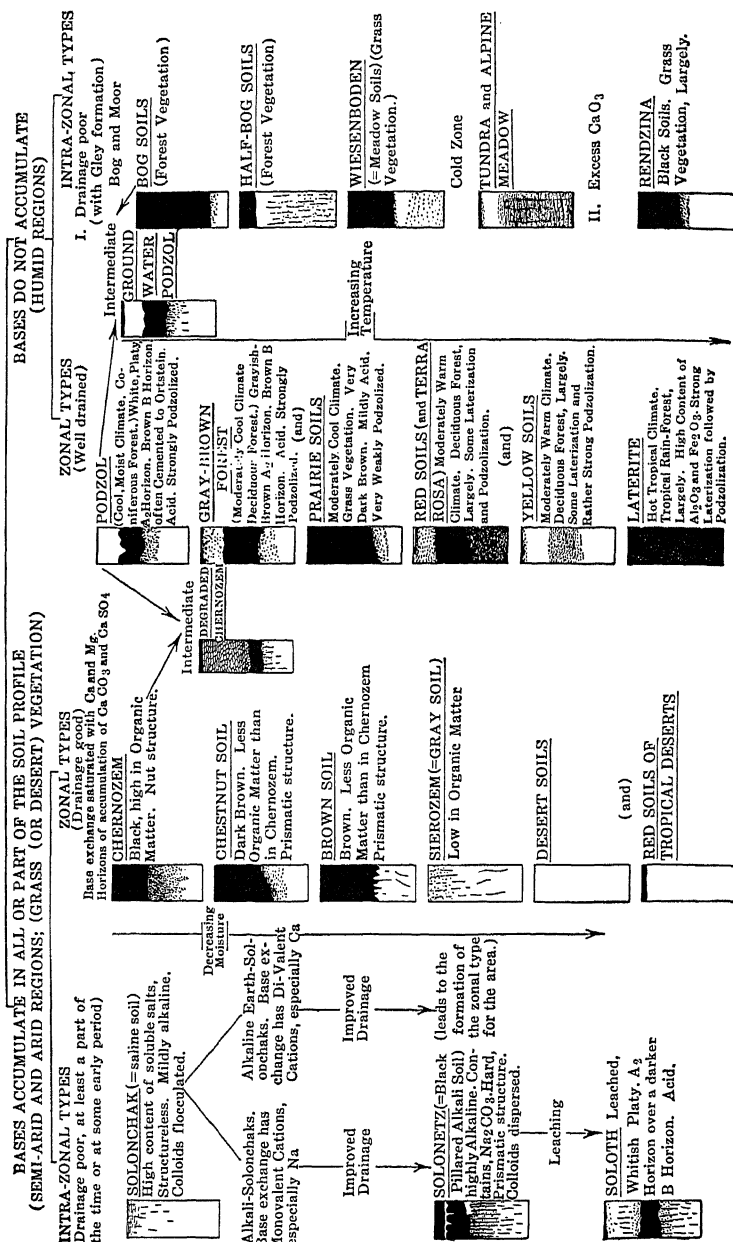


Fig. 15.

## CLAYS

The working properties of clays depend largely upon the size and the degree of dispersion and hydration of their constituent particles, and especially upon the proportion of colloiddally dispersed particles. These factors are in turn influenced by the presence of protective colloids (*e.g.*, humus), salts, and effective reaction (pH value, hydrogen ion concentration). Thus the clay of Mesopotamia is baked into bricks by mere exposure to the sun, whereas straw was necessary to make bricks out of the clay of Egypt (Exodus V). The straw may have been used as a fuel to burn the bricks, or else to improve the working quality of the clay, for patents have been taken out by Dr. Edward G. Acheson for "Egyptianizing" clay by the addition of tannin, extracts of straw and humus, etc. Glue and similar protective colloids deflocculate or "free out" clay and make it "cover" when used in paper-coating or kalsomining.

*Bentonites* are fine clays resulting from the dusts deposited by ancient volcanos. Some varieties form suspensions that readily settle, but others are so highly colloidal that they swell in water just like glue or gelatin. These grades are used for "beauty-clays" and cataplasms, as well as for many technical purposes.

Clay in general is flocculated by acids and by acid or neutral salts. Small amounts of alkalis and of alkaline salts deflocculate it, but larger amounts cause flocculation. Clay slip, prepared with a little sodium hydroxide or carbonate, can be readily poured or cast, even though it contains less water than a stiff mass of clay and water without alkali. On adding a little acid to such fluidified clay slip, the mass immediately becomes so stiff that it will not fall from the inverted vessel.

Clays are very sensitive to small traces of various substances. Thus in the pottery industry certain persons, especially women at times, cannot handle the ware without affecting it. The ancient customs of "treading" the clay with bare feet, and "ageing" it before use, probably involve the introduction of colloids from skin excretions and bacteria, and their effects on the clay. In preparing optically pure "ultra-water" for use in ultramicroscopic research, Zsigmondy found that simple immersion of the finger in such pure water immediately made it show ultramicros.



Each clay as found in nature bears within itself much evidence of its past geological history: the chemical and mechanical processes of past ages; lixiviation by glacial or other waters; subsequent sedimentation in still lakes or flats, or coagulation by saline waters; leaching out of some salts or soluble products; infiltration of other salts and of organic extractives; the pressure of overlying strata; thermal changes due to solar heat, volcanic action, or metamorphic movements of the earth's crust, which may also cause pressure.

Ultramicroscopic examination gives a very good insight into the nature, working properties and impurities of clays. [See J. Alexander: *J. Am. Ceramic Soc.* (1920) 3, 612.] Some idea can be formed of the relative percentage of colloid and coarser particles, and the influence of protectors and coagulating salts traced. Fire clays show the combined effect of the infiltration of protective substances (from peat, lignite or coal deposits) and of salts or acids resulting from the diffusive decomposition of ferrous sulphate (oxidized pyrites). To work properly, clays must have the proper proportion of coarser, finer and colloidal particles, so that by washing and blending clays and working upon them with reagents more powerful than those ordinarily found in nature, we have a wide range of possibilities.

### CERAMICS AND REFRACTORIES

Following the principles above mentioned, the use of alkalis or alkaline salts to deflocculate clay and make a casting slip is general in the ceramic industry. Caustic soda and silicate of soda are largely used. If the clay mixture holds too much water, there will be excessive shrinkage upon drying; and if it is too hydrous, there will be too much shrinkage on firing. In either case the molded article will warp, and this must be prevented by proper selection, mixture and treatment of the clay used. To safeguard against warping, there is often added to the ceramic mixture some powdered burnt clay (broken pottery or grog).

When heated or "burned," clays become irreversibly dehydrated and harden into pottery, bricks, etc. Throughout the whole ceramic process, the pugging, blunging and ageing of the clay, the molding and subsequent drying and burning, may be traced the influence of particle size and impurities, and their effects extend to the zone of actual fusion.

Fire clays have a preponderance of relatively large, consolidated or dehydrated particles, a result which may be brought about in nature by pressure, coagulating salts and a deficiency of organic deflocculators. They take up comparatively little water and therefore do not shrink much on drying. With clays exposed to high temperatures, the chemical composition, which influences the melting point, is vital.

There may be a "eutectic drop" in the case of the admixture of clays, just as there is with metallic alloys. Mixtures for Seger cones are based on the principles above referred to.

In a paper entitled "Glass: the Bond in Ceramics," G. W. Morey states (J. Am. Ceramic Soc., 1934, 17, 145-55): "Refractories are bonded by glass; either a lime glass in the silica refractories, or an aluminum glass in the clay refractories. But a siliceous glass is the characteristic feature which is found in all products of the ceramic art, and glass is the bond which unites the divers ceramic industries."

## FLOTATION

The importance of flotation processes is evident from the fact that in 1918 over 70,000,000 tons of ore were thus concentrated. The understanding of the principles of flotation will be simplified by bearing in mind that, notwithstanding the presence of many disturbing and variable factors, there are involved two main tricomponent systems:

1. *Ore/water/oil*, from which the true ore (usually a sulphide) must emerge with a film of oil which enables it to be taken up by the air bubbles and thus floated off with the froth, while the gangue is wetted and flowed off at a lower level.

2. *Air/water/oil*, which yields the bubbles to float the oiled sulphide.

The oil clings to the sulphide because the surface tension oil/sulphide is less than the combined surface tensions ( $\sigma$ ) water/oil and water/sulphide.

$$\begin{aligned} \text{That is, } \sigma_{OS} &< \sigma_{WO} + \sigma_{WS}, \\ \text{or } \sigma_{WO} &> \sigma_{OS} - \sigma_{WS}. \end{aligned}$$

The oils or some of their constituents distribute themselves at the interface water/air, and thus form stable bubbles, because

the surface tension water/air, exceeds the combined surface tensions water/oil and air/oil.

That is,

$$\begin{array}{ccc} \sigma_{WA} > \sigma_{WO} + \sigma_{AO} \\ 75 & 23 & 33 \text{ (approximate values)} \end{array}$$

The air bubbles forming the froth thus have a more or less stable surface film which is miscible with, though not necessarily identical with, the oil film on the sulphide, for selective adsorption may effect some segregation of the oil constituents. However, the oiled ore particles act like oil; they distribute themselves at the interface water/air, are thus attached to the air bubbles and lifted to the upper froth layer unless they are too heavy or are knocked off.

Some of the complicating factors will now be considered.

*Water.*—Dissolved air aids bubble formation by reducing the internal pressure of the water; so that temperature of the water is important. Most crystalloids, especially acid electrolytes, act beneficially, for they are adsorbed by and coagulate the fine slimes, clay, etc., which then tend to repel the flotation oil. This recalls the old-fashioned household expedient for avoiding the taste of castor oil, by moistening the mouth and throat with orange or lemon juice. Some electrolytes, especially small quantities of alkalis, are very detrimental, because by reducing the surface tension between the water and the oil and the sulphide and the gangue, they tend to emulsify the oil, wet the sulphide and deflocculate the slimes. Humic substances, especially in the presence of alkali, and protective colloids in general, act in like manner; thus glue is very injurious. Colloidal clay or very fine gangue may have a similar action, for they may act as emulsifiers—"fat" clays emulsify oils, tars and asphalts.

*Ore.*—Some ores yield soluble substances which exert an effect, but as a rule the fineness of grinding is the most important factor. While the gangue must be fine enough to flow off readily under the conditions of operation, it should not be so fine as to cause the undesirable emulsification above referred to. The sulphide particles, if too large, are not lifted or are readily knocked off; if too small the bubble surface is covered by too small a weight of ore, and there is great loss in efficiency. The tiny ore particles

should make a substantial armadillo-like covering about the air bubbles, which aids in the stabilization of the bubbles.

*Oil.*—Many substances used in flotation—*e.g.*, cresols—are not oils at all, and many substitutes for oil have been patented. The rapid development of the flotation industry created a sudden demand for materials like pine oil which previously had a limited demand, and markets were thus turned topsy-turvy. Mixtures of substances may be used as “oil,” for the foam-producing and the sulphide-oiling factors are not necessarily identical. The percentage of oil is also important from an operative as well as from a patent standpoint.

The whole question of flotation demands intensive study and experience. Thus Callow estimates that with four different oils, three different oil percentages, two pulp densities and two temperature changes, there are possible about 60,000 different combinations of conditions.

Some of the principles involved in flotation had long been utilized. The natives in the Far East (Phillipines) when panning for gold, often squirt the juice of “gogo bark,” which they chew, into the pan in order to deflocculate the accompanying clay. In the diamond fields the water dispersion of the “blue ground” is allowed to flow over an inclined table coated with grease. The diamonds tend to stick preferentially to the grease because they are “wet” by it, while the quartz and other minerals pass on with the water.

The slurries formed when coal is washed must be flocculated in order to avoid nuisance and to recover the fines. E. T. Wilkins (J. Soc. Chem. Ind., 1935, 54, 391-3T) finds that in many cases at least, hydrophylic colloids (starch, gelatin) are much superior to electrolytes as flocculators, especially for larger particles. Apparently the colloids are adsorbed by the coal particles, forming surfaces which cohere, binding the particles into a coherent floc of sufficient coarseness to settle out. Quite a number of surface-active substances (*e.g.*, Turkey-red oil, castile soap, cresols, sodium xanthate and “wetting-out” agents), when used in certain *minimal minute amounts*, were found to sensitize the coal slurry to subsequent flocculation by gelatin or starch, whose fixation is evidently thus facilitated. (See also p. 154; and J. O. Samuel, Chemistry and Industry, 1936, 55, 669-80; and I. Traube, Trans. Faraday Soc., 1935, 31, 1737). Traube terms gelatinous col-

loids *flotation poisons*, since they may displace oil and remove ores from the foam. When adsorbed, they may bind the particles on which they are fixed into flocculates which settle out. They thus resemble cohesive colloids (see p. 322).

## CHAPTER XI

### PRACTICAL APPLICATIONS (*Continued*)

#### DYEING

FOUR principal theories of dyeing have held the field: (1) The mechanical or physical theory; (2) the chemical theory; (3) the colloid-diffusion and adsorption theory; (4) the electrical theory. A complete historical review of these theories, with bibliography, is given by P. E. King in the First Report on Colloid Chemistry and Its Industrial Applications, published by the British Assoc. for the Adv. of Science, London, 1917. Alexander's "Colloid Chemistry," Vol. IV, contains papers expounding different aspects of dyeing, by G. von Georgievics (Prague), Wm. Harrison, and Prof. Wilder D. Bancroft (Cornell University).

There are many different types of dyes and thousands of different individual dyestuffs, and the various fibers, tissues, etc. (cotton, silk, wool, linen, jute, straw, paper, wood) all react characteristically. The phenomena of dyeing are, therefore, very numerous and complicated. In essence the conflicting theories are not so divergent as might be imagined; they differ mainly as to the classification of the attractive force between substrate and dye.

Since all forces of the nature involved are ultimately due to electro-magnetic fields of the atoms involved (or of their electrons), the attraction is essentially electrical or chemical; but since this attraction is exhibited only when the dye and substrate expose sufficient active free surface, the operation is "physical" or "colloidal." In commenting on a large group of compounds built up of increasing numbers of benzene nuclei, Dr. R. Fraser Thompson (Chem. and Ind., 1936, 55, 86) observes: "Affinity (for cotton) begins to appear as the molecule becomes more complex by the addition of further benzene rings." Apparently, the more complicated compounds can "seat" themselves to the fiber structure. The compounds formed do not in general possess

that preciseness connoted by the present meaning of the expression "chemical compound," unless very tiny areas are considered.

In some cases the colloid fiber adsorbs the dye, as with basic colors which dye silk and wool directly. In other cases there is necessary a *mordant*, which is first adsorbed and then fixes the color; *e.g.*, for some dyes cotton must first be mordanted with an insoluble colloid precipitate formed *in situ* by tannin and tartar emetic. Certain dyes of opposite charge may mutually precipitate each other, and thus serve as mordants for each other; *e.g.*, methylene blue and dianil blue 2 R; patent blue V and magenta. But a large excess of either dye may serve as a colloidal protector and either prevent the precipitate or make it colloidal. Grüber's stains owe their peculiar properties mainly to colloidal impurities (dextrin, etc.), so that the same dyes when spectroscopically pure, work differently.

Ultramicroscopic examination reveals the fact that many dyes are colloidal in solution, and the selective coloring of fibers, tissues, cells, nuclei, etc., in some cases probably represent the selective adsorption or precipitation of one colloid by another, a view sustained by the ultramicroscope researches of N. Gaidukov. Some dyes can be extracted from the dyed fiber by alcohol, which would hardly be the case if a true chemical compound were formed. There is an optimum degree of dispersion for each dye [zone of maximum colloidalness (see p. 35)]. This is shown by the work of R. Auerbach [Kolloid Zeit. 1924, 34, 109] which indicates that if too coarse, the dye lacks diffusive power; and if too fine, it passes out of the fiber once more. (J. Alexander, Am. Chem. Soc. Washington Meeting, 1924; Am. Dyestuff Reporter, 1934, 23, 668-80.) Temperature, and the addition of salts ( $\text{Na}_2\text{SO}_4$ ), acids, colloidal protectors (boiled off silk liquor) and the like are used by practical dyers to control the degree of dispersion.

Colloid chemistry also throws much light upon many obscure points in the practical art of dyeing. It is possible to obtain much more level colors in old dye liquors than in fresh ones, and here it seems that colloiddally dissolved substances are responsible, exercising a restraining action upon the absorption of the color. The addition of Glaubers' salt facilitates level dyeing, probably by its action as an electrolyte, producing a partial coagulation of the dyestuff, so that the particles of the latter, thereby made

larger, are absorbed more slowly and evenly—the dye does not “rush” onto the fiber.

Congo red when dyed on silk or wool changes only in shade if the fiber is dipped in dilute sulfuric acid, whereas when dyed on cotton it turns blue in like circumstances. Upon following ultramicroscopically the changes produced in colloidal aqueous solutions of benzopurpurin, J. Alexander found [J. Soc. Chem. Ind. 1911, 30, 9] that the color change was accompanied by an aggregation of the dye ultramicros. If a protective colloid such as glue was added to the dye solution before the addition of acid, the dye ultramicros did not aggregate, and the color change could thus be modified or prevented. It seems, then, that silk and wool exercise a greater protective action on the adsorbed dye than does cotton, which harmonizes with the fact that proteins are in general better protectors than carbohydrates. This is also evidence against the chemical theory of dyeing in this case.

### SHOWER-PROOFING FABRICS

If textile fabrics and the like are coated with a surface film of wax, aluminum stearate and so on, they are not wet by an ordinary shower, whose drops roll off “like water off a duck’s back.” With an untreated fabric the attraction between the fabric and water bursts the surface skin of air on the fabric and the surface film of the raindrop, which then spreads itself out on the fabric and is absorbed into its pores.

Remembering that as the attraction between surfaces increases the surface tension between them decreases,\* this means that wetting occurs when the surface tension ( $\sigma$ ) water/fabric is less than the combined surface tension water/air and air/fabric. That is,

$$\sigma_{WF} < \sigma_{WA} + \sigma_{AF}, \dagger$$

$$\text{or } \sigma_{WA} > \sigma_{WF} - \sigma_{AF},$$

Since surface tension is only “skin deep,” the surface tension water/fabric really becomes that of water/wax and is greatly increased. Therefore,

\* In fact, when the surface tension in a two-phase system becomes zero, solution or colloidal dispersion may occur.

† W = water, F = fabric, A = air,  $\sigma$  = surface tension.



$$\begin{aligned} \sigma_{WF} &> \sigma_{WA} + \sigma_{AF}, \\ \text{or } \sigma_{WA} &< \sigma_{WF} - \sigma_{AF}, \end{aligned}$$

the water is repelled and no wetting occurs.

### NITROCELLULOSE AND ITS PRODUCTS

When cellulose (cotton, purified paper pulp) is soaked in a mixture of nitric and sulphuric acid, it takes up from 10 to 13 per cent. of nitrogen, depending upon the purity and moisture content of the cellulose, the exact composition of the acid bath and the time and temperature of nitration. The formation of a series of cellulose nitrates is generally assumed, although A. Müller suggested the existence of adsorption compounds. In any event the acid fixation curve is continuous, notwithstanding numerous attempts to separate out definite nitrates. Cellulose has a structure, the interior of a cotton fiber being less dense than the exterior, and since the nitration starts at the surfaces and leaves them comparatively undisturbed, its course will evidently be dependent upon the amount of free surface exposed. It has been found that by intensive grinding cellulose yields a colloidal solution in water.

The colloidal solutions that result from dissolving cellulose nitrate in various solvents or mixtures, are widely used as varnishes and lacquers to coat patent and artificial leather, metals, etc. Their degree of dispersion and therefore their viscosity is dependent upon the nature of the solvent, whose action may depend upon small percentages of substances which exercise a peptizing action. Thus old patents claimed that nitrocellulose dissolved in wood alcohol, because the "wood spirit" of those days contained ketones; the nitrate is insoluble in *pure* methyl alcohol. According to F. Sproxton [Third Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1920], if water be added in gradually increasing quantities to an acetone solution of cellulose nitrate, keeping the percentage of the solute constant, the viscosity rises to a maximum (both absolutely and relatively to the viscosity of the solvent) and then falls until it is practically the same as that of the solvent. This seems to be another illustration of the zone of maximum degree of colloidality [see J. Alexander, J. Am. Chem. Soc. 1921, 43, 434], for the Tyndall effect becomes marked close to the position of maximum viscosity. Modern lacquers are formulated

upon "low viscosity cotton," produced by chemical fragmentation of the more composite "molecule," usually through the action of alkali.

### CELLULOID

This is a transparent gel formed when nitro-cellulose is kneaded with alcohol and camphor. In the subsequent sheeting, pressing and molding operations it undergoes a slow syneresis due to the loss of the alcohol and some of the camphor. Schüpphaus [Thorpe's Dict. Appl. Chem., Vol. 1] thinks that there is some kind of chemical combination between the camphor and the nitrocellulose because the heat of combustion of the two ingredients is greater than that of celluloid itself. This, however, is no criterion, for as Prange has shown [Recueil des Trav. Chim. des Pays Bas, 9, 121 (1890)] colloids may set free heat if their particles aggregate, and heat is liberated when nitrocellulose and camphor are mixed. Furthermore, according to Sproxton, the optical rotation of a dilute acetone solution of celluloid equals the sum of the rotations of its two ingredients.

The view of Dubosc [Le Caoutchouc et la Gutta Percha, 1919, 16, 9803] that celluloid is a camphorgel (nitrocellulose dispersed in camphor) seems well warranted by the facts. Its plasticity on heating to 80 deg. C. is attributed to the fusion of the dispersion medium, camphor, which diminishes the internal friction. The fact that camphor constitutes only about one-third the bulk of the celluloid does not militate against this view (as Sproxton suggests), for S. U. Pickering was able to emulsify 99 per cent. of petroleum oil in 1 per cent. of soap solution, obtaining an almost solid emulsion.

### EXPLOSIVES

The modern propellant explosives consist of nitro-cellulose colloided with ether/alcohol, nitroglycerin, etc. The rate of burning of the grain is intimately connected with the external and internal surfaces of the explosive, the former being controlled by the size, shape and perforations of the pieces, and the latter by careful regulation of the manufacturing process. Variations in the original cellulose, the process of manufacture and the presence of traces of impurities may materially alter the stability

and ballistic properties of the product as well as the viscosity of its solutions.

Blasting gelatin is a colloidal gel of 7 to 8 per cent. nitrocellulose with nitroglycerine, the former probably being the dispersed phase. There is evidently an optimum internal structure for this colloid, since its tendency to become insensitive on ageing is a bane of the manufacturer. The use of a protective colloid seems indicated here; it will also probably tend to prevent the exudation of the dangerous nitroglycerine, which is especially apt to occur on freezing, and constitutes a serious danger on thawing or subsequent handling.

### PAINTS, PIGMENTS, VARNISHES

When linseed oil, China wood oil, etc., begin to polymerize upon boiling, they form *isocolloids*, that is, a dispersion of the polymerized in the unpolymerized oil. Highly boiled China wood oil sets to a gel. The various varnish gums go into colloidal dispersion, and it seems not improbable that they may act as protectors to the boiled oil, keeping it from gelatinizing. What is known as the "break" in boiled oils is the coagulum resulting from the albumin, etc., which must be filtered or settled out.

*Varnishes* must possess a very fine internal structure when dry, for they permit the swelling of gelatin protected by the varnish film. In most cases the internal spaces permit the formation of a cloudy dispersion or emulsion of water in the film, but with the most highly protective varnishes they are so fine that although as much as 5 per cent. of water be taken up, the film remains clear. The impermeability of the varnish film to most salts indicates the fineness of the pores; but since water absorption increases with diminishing salt concentration, it would seem that the salt by adsorption or swelling causes a diminution of the size of the pores. Normal solutions of  $\text{NaCl}$ ,  $\text{MgCl}_2$  and  $\text{CaCl}_2$  prevent the ordinary varnish film from turning white, and greatly diminish the amount of water passing through.

*Shellac* contains about 4 per cent. of wax, which goes into colloidal dispersion in most solvents. In solutions over about  $3\frac{1}{2}$  lbs. per gallon the wax does not readily settle out, but weaker solutions show a separation of wax-free "*French varnish*" or clear shellac solution.

*Pigments* vary greatly in their degree of dispersion which vitally controls their opacity, surface covering power, and oil-absorbing capacity. Because of the importance of the physical condition, mere chemical analysis is quite insufficient to rate pigments. The most finely subdivided oxide of zinc commands the highest price, chromates of lead vary in color from lemon yellow to orange and Prussian blues vary in shades as their particle size changes. The difference between blanc fixe (precipitated  $\text{BaSO}_4$ ) and ground barytes is enormous. Too great a degree of dispersion is harmful, for there is an optimum degree of dispersion on either side of which desirable properties begin to diminish. The cross-precipitation of  $\text{BaS}$  by  $\text{ZnSO}_4$  yields a product so highly colloidal that it is furnace-dried and powdered to produce a more compact lithopone. The fact that a mixture of blanc fixe and zinc sulphide does not give the same degree of opacity as lithopone indicates that in the latter there is a close adsorption. Generally in making precipitated colors or color bases the degree of dispersion is controlled by temperature, colloidal or other protectors (or even coagulants), and the concentrations and speed of mixing of the reacting solutions. [See H. A. Gardner, J. Ind. Eng. Chem. 1916, 8, 794.]

While *paints* are essentially mixtures of pigments, drying oils, and solvents, the presence of small amounts of other substances may be highly desirable. Thus E. G. Acheson [J. Soc. Chem. Ind. 1921, 30, 1426] states that the addition of a minute amount of tannic acid causes a pigment to deflocculate readily on grinding in oil, and the use of about 2 per cent. of water emulsified by such a substance as silicate of soda has long been common in mixed paints to prevent hardening or settling in the can. Ware and Christman [J. Ind. Eng. Chem. 1916, 8, 879] found that the addition of aluminium palmitate or oleate to paints helps this condition; these non-aqueous protective colloids aid in keeping the pigment in suspension, partly because they increase the viscosity of the oil. These authors also investigated the "livering," puttying, and skinning of mixed paints. Livering is attributed mainly to the formation of a zinc soap gel, the formation of which is aided by the presence of zinc resinate (formed from rosin used in the paint) and acid pigments.

An interesting application of colloid chemistry was made by Wheeler P. Davey, of the General Electric Co., who made a

"water japan" by emulsifying japan base (mainly a solution of asphalt in a drying oil) in water containing ammonia and a protective colloid. Besides being cheaper and less hazardous than the ordinary japan made with petroleum solvents, the water japan is much less viscous and small pieces of metal may be coated by first heating them and dipping them *en masse* in baskets into the emulsion. As the "japan" particles are negatively charged, they may also be deposited on the metal by making it the anode in an electric circuit. In both cases the japan base attached to the metal is free from solvent, and is baked as usual; "secondary drip" and scars due to mutual contact between the metal pieces are largely avoided by the wide latitude permitted in the composition of the base, for these changes do not seriously affect the viscosity of the emulsion.

### EMULSIONS

As with other dispersions, emulsions may be made by aggregation as well as by dispersion methods. Thus emulsions of benzene may be made by condensation of its vapor in a suitable dispersion medium (Dr. C. G. Sumner, University of Manchester); and the formation of emulsions by dilution of alcoholic solutions has been referred to on p. 38. Commercially, dispersion methods are mainly used, and quite a variety of different machinery is employed, some of it working on the batch principle, some of it by continuous flow. *Time* is required for the adsorption and stabilization of a protective film about the droplets of the dispersed phase after they are formed mechanically, and a sufficient concentration of the "stabilizer," without too great viscosity, is desirable. The presence of a gas phase, as by air-bubble agitation, is usually undesirable for the stabilizer may accumulate at the air/water interface where it is not wanted, and be removed from solution with the froth thus stabilized (Ramsden effect).

Besides high-speed propeller and similar stirring agitators, very fine dispersions have been secured with *homogenizers* or *viscolizers*, introduced initially into the dairy industry to effect finer dispersion of the fat naturally emulsified in milk. The initial emulsion is forced under high pressure (up to about 5,000 lbs. per sq. in.) past the seat of a special valve, against the pressure of a powerful spring. Homogenization results in a considerable

increase of viscosity, often accompanied by a clumping of the new droplets which is broken by passage through another valve or valve part, with a drop in viscosity. The clumping seems due to residual forces (see p. 34) at the newly formed interfaces being satisfied by mutual attraction of the droplets, *before* adsorption of the stabilizer can interfere. The British Mayonnaise Manufacturers' Association (Proc. Third Annual Convention, 1928, p. 19) found that while the three colloid mills which they tested may be serviceable in making salad dressing with 50% oil or less, they were not suited for heavier mayonnaise, and in some cases actually broke down what emulsion was formed.

The preparation of stable emulsions is of importance in pharmacy (cod-liver oil, etc.) and cookery (mayonnaise, hollandaise sauce, etc.); and the biological importance (myelins, nerve tissue, fat depots, etc.) is obvious.

The "breaking" of undesirable emulsions (de-emulsification) is also of considerable practical importance. Thus many petroleum products contain large amounts of emulsified water which must be removed. The basic method of F. G. Cottrell [U. S. P. 287,115 (1911)] makes use of high tension electric current [for details see J. Ind. Eng. Chem. 1921 13, 1016]. Besides this filtration, chemical, and centrifugal methods are used to break the interfacial films and permit the droplets to coalesce. In some cases even as little as 0.001 per cent. of a protective colloid will do this, by coagulating the emulsostatic film. Freezing does the same thing in other instances. For further details see W. Clayton's book on "Emulsions and Emulsification," Blakiston, 1923, and his paper "The Preparation of Emulsions," Chemistry and Industry, 1932, 51, 129-139. See also p. 212.

## CHAPTER XII

### PRACTICAL APPLICATIONS (*Continued*)

#### SOAPS AND DETERGENTS

THE orthodox view that soaps are simply alkali salts of fatty acids was considerably shaken when Lewkowitsch [J. Soc. Chem. Ind. 1907, 26, 590], after epitomizing the views of Merklen, said:

"But whatever may be the outcome of renewed experiments, Merklen's views cannot fail to stimulate further research into the composition of soap, and thus help raise the industry of soap-making, which has too long been looked upon as a mere art, to the rank of a scientifically well-founded industry, the operations of which are governed by the laws of mass action, the phase rule, and the modern chemistry of colloids."

Merklen's views which aroused this comment are that commercial soap is a product of essentially variable composition which depends on (1) the nature of the fatty acids, (2) the composition of the 'nigre' (in the case of settled soaps), (3) the temperature at which the boiling is conducted. It behaves like a colloid, and should not be regarded as a compound of fatty acids having chemically combined a definite amount of water, but is rather an "adsorption product" whose composition depends upon the environment in which the fatty acid salts find themselves at the moment of the finishing operation.

According to J. W. McBain [Third Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1920], homogeneous solutions of soap are rarely met with during the process of manufacture, since their viscosity would be prohibitively great, and must be held in check by the addition of caustic soda, salt, or other electrolytes, to bring the soap into a gel or even into coagulated form (soap curd). The soap is usually in the form of a dispersion of two soap solutions, soap-in-water, and water-in-soap, and may exist in the form sol/sol, sol/gel, or sol/curded-gel.

Most commercial soaps are of the sol/curded-gel type, but soft soaps may be of the sol/gel type. McBain regards soaps as *colloidal electrolytes*, that is, as salts in which one of the ions has been replaced by a heavily charged, heavily hydrated ionic micelle which exhibits a high conductivity. (See paper by J. W. McBain in Alexander's *Colloid Chemistry, Theoretical and Applied*, Vol. I, pp. 137-164.)

Martin H. Fischer ["Soaps and Proteins"; "The Lyophobic Colloids," by M. H. Fischer and Marian O. Hooker (C. C. Thomas, 1933)] has shown that the hydration capacity of soaps varies greatly with change in the fatty acid, and the base. Some soaps hold enormous amounts of water, while others hold very little, so that if the amount of water present exceeds the hydration capacity of the soap, free water separates or may remain emulsified (see p. 405).

Most soaps form crystalloidal solutions in alcohol, which ultramicroscopically are quite clear; but if a droplet of tincture of green soap, for example, be allowed to diffuse into a clear field of pure water held between a slide and cover glass in a dark-field condenser, the soap practically explodes into numberless actively moving ultramicros. The colloidal nature of aqueous soap solutions is further indicated by their turbidity, viscosity, and gelatinization.

The *detergent action* of soap is due to its ability as a colloid to produce deflocculation. Hillyer [J. Am. Chem. Soc. 1903, 25, 511, 1256] showed that this action is not due to alkali freed by hydrolysis, and that alkali itself does not wet oily matter. But all "dirt" is not oily, and W. Spring [Kolloid Zeit. 1909, 4, 161; 6, 11, 104, 164] in experiments with purified lamp-black, iron oxide, alumina and silica, showed that soap makes such particles less adherent to the fabric, and to each other. The attraction of both fabric and "dirt" for soap exceeds the attraction of the fabric for "dirt" and of "dirt" particles for each other. In order that the soap may be adsorbed at the interfaces involved, it must be in colloidal dispersion, which requires hot water in the case of many soaps.

The practical working properties of various commercial soaps depend mainly upon the nature of the fatty acids in them. Thus sodium oleate is much more readily dispersible in water to colloidal dimensions than is sodium stearate, and even small amounts



of oleate materially assist the higher fatty acid soaps to dissolve. In fact mixtures of fats or fatty acids show a "eutectic drop" in melting point, just as do alloys. From the oriented wedge theory of emulsions (see p. 106) it is evident that in an emulsion of oil in water, potassium soaps, having larger molecules (K) turned to the water phase than the sodium soaps (Na), tend to make a foam with smaller bubbles, which is therefore more stable. For this reason shaving soaps consist largely of potassium soaps. Triethanolamine also yields soaps much used in cosmetics, emulsions, etc.

H. Jackson [Cantor Lecture, J. Soc. Arts, 1908, 55, 1101] examined microscopically the supernatant fluid resulting from washing a piece of dirty cloth with soap and water, and found in it countless particles in a state of oscillatory motion ("*pedesis*"). This is really *Brownian motion*, first noted by the English botanist Robert Brown in particles approaching the limit of microscopic resolvability. The ultramicroscope shows it to be largely due to bombardment of these larger particles by the still smaller and more actively moving colloidal particles, which in turn are activated by the motion of still smaller particles (water molecules), and so on. When an individual fiber was bathed in soap solution, the dirt particles gradually loosened and began to oscillate. Upon substituting salt solution for the soap, the particles flocculated and the motion ceased. An ultramicroscopic examination of the detergent action of soap is very interesting.

While soap is cheap, and has good wetting-out and emulsifying properties, it is sensitive to acids and salts, especially to lime and magnesia salts found in "hard" water, which precipitate out insoluble soaps. It has been found that the sodium salts of the sulfated higher fatty alcohols have superior wetting-out power, and withstand both acids and lime, besides being good emulsifiers. For example, lauric acid, from coconut oil, is hydrogenated to lauryl alcohol. The alcohol is then sulphonated and converted into the sodium salt. Mixtures of the various sulphonated alcohols are generally found in the commercial products, which are sold under different trade names, *e.g.*, Avirol, Gardinol, Dreft, Duponol. Other compounds with similar properties are also on the market, and in increasing numbers.

These products have found extensive use in the processing of cotton, wool, silk, and rayon, as well as in the field of cosmetics.

Many other substances are used or recommended for wetting out, as the indices of Chemical Abstracts indicate. Sodium pyrophosphate and hexametaphosphate ("Calgon" is mainly the latter) are used to prevent the precipitation of lime soaps. Sulphonated oils and pine oil-soap combinations also have their uses. Many conditions must be considered before deciding what is the best of the many products offered by science and industry for a certain purpose.

In addition to their detergent action, which washes away bacteria, Walker (J. Infect. Diseases, 1925, 35, 557; 37, 181; 1926, 38, 127) found that soaps of the higher fatty acids, which are markedly colloidal, exhibit considerable bacteriocidal power, which naturally varies with different bacteria. Against pneumonococci, sodium laurate was more powerful than phenol. Staphylococci are very resistant. Typhoid, paratyphoid, colon, and dysentery bacilli are relatively resistant to the soaps of unsaturated fatty acids, but succumb to soaps of saturated acids from stearate up. (See p. 38.)

*Transparent soaps* are made by keeping the dispersion of the particles of the finished soap well toward the lower limit of colloidal dimensions. Among the factors that produce this effect are (1) the selection of the fatty acids; (2) quick chilling; (3) protective colloids; (4) the addition of alcohol, glycerol, sugar and the like, which tend to dissolve the soap crystalloidally. Frequently some of the fatty acid salts crystallize out in the clear matrix, marring the commercial appearance of the soap, and these crystals exhibit the dendritic or ramifying tendency common when crystallization occurs in the presence of colloids. W. D. Richardson [J. Am. Chem. Soc., 1908, 30, 1414] found that the fatty acids separated from the crystals had a higher melting point than those separated from the clear matrix.

To demonstrate the effect of the speed of chilling on particle size, J. Alexander melted a piece of commercial transparent soap and cast it into two cups, one of which was instantly chilled with ice, while the other was allowed to cool slowly while immersed in hot water. The quickly chilled piece was transparent and upon ultramicroscopic examination showed much smaller ultramicros than the slowly cooled piece, which was opaque. After several months standing the quickly chilled soap still appeared clear, whereas the other had large opaque spots. Upon ultramicro-

scopic examination the transparent piece appeared as before, but the slowly cooled piece showed perfectly resolvable crystals in a clear matrix.

### ADHESIVES

The adhesive industry is, in a modest way, a key industry. There is hardly an article or material connected with our daily life which does not call for the use of adhesives in its production or distribution. Adhesives are used to make such diverse things as cradles and coffins; pianos, paper boxes and pocket-books; furniture and fabrics; books, matches and airplanes. Packages of all kinds are labeled with adhesives and cartons are closed by them. Adhesives seal untold millions of envelopes and affix postage and revenue stamps. In abrasive papers, cloth, belts and wheels, the sand, garnet, emery, carborundum or other cutting powder is held fast by adhesives. Many sizings are adhesives or contain adhesives.

The main commercial adhesives fall into three groups: (1) *carbohydrate adhesives* (gums, flours, starches, dextrans); (2) *protein adhesives* (glue, gelatine, casein, egg and blood albumens, soya-bean protein); (3) *mineral adhesives* (e.g., sodium silicates). Concentrated solutions of low-viscosity nitrocellulose, of "masticated" rubber, and of resins like shellac, as well as synthetic resins, are also largely used.

For special purposes adhesives are compounded of a variety of materials to secure desirable working properties for the mixture under the widely varying conditions of practical use. Speed of "tack" or hold, speed of set or drying, and behavior on ageing, exposure to dampness, rodents, insects, mould, etc., are all of importance.

Our principal adhesives, such as gums and glues, are substances which because of the makeup of their molecules possess powerful residual fields of force and are therefore capable of attaching themselves to other substances possessing residual fields of the opposite charge. They must besides have sufficient residual force to cling powerfully to adjacent molecules of their own kind. Thomas Graham long ago remarked that colloids as a rule adhere better to each other than to crystalloids. One reason probably is that colloids possess a plurality of residual fields which may

have different charges at different points. They are also highly polar.

Adhesion is purely a matter of surfaces. Glue will stick paper to wood, but not to paraffin or to wood having a paraffined surface. It is true that glue will hold paper to paraffin or to bright tin until the adhesive dries; then the powerful attraction of the glue particles for each other as they are dehydrated breaks the weak bond between the glue and the paraffin or metal, although it is unable to break the bond with the paper to which the other face of the glue layer clings tightly.

### LUBRICATION

The automobile has brought such an increase in the consumption of petroleum that a material curtailment in supply, if not actual exhaustion, lurks in the not far distant future. But we may look with confidence to colloid chemistry to supply the lubricants of that day.

The principle involved in lubrication is the maintenance, on each of the surfaces in contact, of an adsorbed layer of an easily deformable substance (usually a fluid) so that the surfaces can not come into actual contact, or "seize." Since the attractive forces at surfaces depend on their residual electrical fields, lubrication is affected by the chemical and physical nature of the surfaces as well as by that of the lubricant. Good lubricants are so strongly adsorbed that great pressure and speed are necessary to tear them loose; they place *the plane of slip or shear* within the lubricant itself.

W. B. Hardy\* [J. Soc. Chem. Ind. 1919, 38, 7 T] made some illuminating experiments with glass, which absorbs from the atmosphere rather more of its impurities than of the elementary gases, yielding a film about 1 millimicron ( $1 \times 10^{-7}$  cm.) thick, that Lord Rayleigh termed "grease" because it has the properties of an oil. This "grease" tends to make pipettes and burettes deliver inaccurately, so analytical chemists remove the absorbed layer by oxidation with bichromate and sulphuric acid.

For the same reason new or raw glass surfaces have mechanical properties different from those of a satisfied or neutral

\* See also his splendid paper in Alexander's Colloid Chemistry, Theoretical and Applied, Vol. I (1926).

surface. Thus a finger bowl or tumbler does not give a musical note when rubbed with the wetted finger, unless the "grease" film is removed by vigorous rubbing with the finger tips until a peculiar clinging feeling is felt, due to "seizing" between finger and glass.

Experiments with cleaned glass surfaces have shown that water, ether, alcohol, benzene and strong ammonia do not prevent "seizing" even if the surface be flooded with them. A thin film of glycerin did not lubricate, but flooding the glass surfaces reduced the tangential force required to move them from 55 grams to 9 grams. Most acids, for example, sulphuric, acetic, oleic, lubricate better in thick layers.

Because animal oils, such as sperm or lard oil, are more highly adsorbed by metal surfaces than are petroleum oils, they have long been blended with the latter in considerable quantity to improve the lubricating value. It has been found, however, that such additions owe their value largely to the free fatty acids present which are highly adsorbed, and Southcombe and Wells patented the addition of about 1 per cent. of such acid to mineral oils, thereby effecting a great saving, by avoiding the cost of the blending oils. An X-ray investigation of "addition agents" to lubricants is described by Geo. L. Clark, R. R. Sterrett, and B. H. Lincoln (Ind. Eng. Chem., 1936, 28, 1318-28).

Colloidal graphite has won for itself a place in lubrication, as an addition to oils. It is firmly held by metal and readily wet by oil. In 1907 when Dr. Edward G. Acheson first exhibited his "deflocculated graphite," the writer recognized it as colloidal graphite, and later exhibited to its inventor its intense kinetic activity in the ultramicroscope. (See paper by Dr. Acheson in Alexander's Colloid Chemistry, Vol. III, p. 547-54.)

Most *lubricating greases* are colloidal oil/water emulsions stabilized with sodium or calcium soaps. B. B. Farrington and W. N. Davis (Ind. Eng. Chem., 1936, 28, 414-6), by ultramicroscopic (dark-field) examination, have correlated the texture of lubricating greases with the fiber-length of the soaps (Ca, Al, Pb, Na, Zn) dispersed in them. Their classification follows:

<i>Class of Fibers</i>	<i>Fiber Length, in <math>\mu</math></i>	<i>Texture of Grease</i>
Long	100 or more	Fibrous, ropy
Medium	10 to 100	Clinging, slightly rough
Short	1 to 10	Slightly rough, short
Micro	1 or less	Smooth, unctuous

The so-called "*cutting oils*" which form stable emulsions with water are made by mixing petroleum with water-soluble protective oils like turkey-red (sulphonated) oil. The thrust boxes of steamers which absorb the tremendous pressure of the propellers are lubricated and cooled by circulating an emulsion of oil and water.

The *viscosity of oils*, which is an important factor in lubrication, seems to depend to a considerable extent on the degree of molecular aggregation. Thus Dunstan and Thole (J. Inst. Petrol. Tech. 1918, 4, 191) found that mineral and fatty oils show an exceedingly fine heterogeneity in the ultramicroscope which they attribute to iso-colloidism.

### COAL

Coal as the end product of a colloidal transformation, was first considered by Thomas Graham (see p. 151).

In recent years the complicated structure of coal has been given much attention. In banded bituminous coal the following constituents are recognized (M. C. Stopes, Proc. Roy. Soc. B, 1919, 90, 470):

*vitrain*, brilliant, with conchoidal fracture.

*durain*, dull, hard coal.

*clarain*, bright coal.

*fusain* ("mother of coal" or "mineral charcoal"), is the most friable portion whose fineness controls the speed with which combustion spreads in the mass. When very fine it absorbs oxygen with avidity, and this may be a factor in *spontaneous combustion*.

Stopes and Wheeler (Monograph on Constitution of Coal, Brit. Dept. Sci. Ind. Res. 1918) define ordinary coal as a compact, stratified mass of mummified plants (which have suffered arrested decay to varying degrees of completeness), free from all save a very low percentage of other matter. Although coal retains to some extent the structure and general chemical nature of the original plants, the presence in peat of Dopplerite (a dark, apparently structureless jelly) indicates that part of the coal was probably in this state, which may account for some of the adsorbed substances found in coal.

Reinhardt Thiessen (U. S. Bureau of Mines, Bull. 117; Journ. of Geology, 1920, 28, 185-208), divides the main con-

stituents of coal into (1) *bright* or *glanz* coal, (*antharyxalon*) compact, pitchy jet-black, and of conchoidal fracture, formed from undisintegrated trunks and large limbs and retaining the original woody structure, and (2) *dull* or *matt* coal, less compact, dull grayish, and showing an irregular fracture; consisting of numerous small layers or chips of *anthraxylon* embedded in a dull matrix, the *attritus*, which is derived from assorted vegetable residues.

In the very nature of things, classifications of coal constituents must be rather arbitrary, but it is evident that the sub-microscopic structure of coal has much to do with its practical working properties.

Coal contains small amounts of many elements, disregarded in most analyses, which are found in the ash. These may affect the practical properties of the coal by acting as catalysts, as fluxes for the ash, etc. (See V. M. Goldschmidt, Ind. Eng. Chem. 1935, 27, 1100.)

#### "COLLOIDAL" FUEL\*

"Colloidal" fuel consists of finely powdered coal, cheap tars and the like, dispersed in mineral oil and stabilized by a protective colloid or "fixateur" such as lime soaps or resinates, so that it may be stored, piped, atomized and burned practically like oil itself. As this new composite fuel may at one stroke relieve the drain on the earth's rapidly diminishing stores of petroleum, and lead, as well, to the utilization of coal waste (culm, screenings), inferior fuels (peat, lignite), and even cellulose waste (slabs, sawdust), it may become a material factor in the conservation of our natural resources.

Coal or other combustible solid is prepared for dispersion by being pulverized so that about 95 per cent. passes through a 100-mesh screen, and 85 per cent. through a 200-mesh screen. This means, of course, that the bulk of the weight is in particles hundreds and thousands of times larger than colloidal dimensions. But the violent motion of colloidal particles aids in maintaining the Brownian motion of larger particles which helps to keep them

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\* A paper on this topic was presented before the Institution of Chemical Engineers (London) on Feb. 21, 1936, by Dr. A. B. Manning and R. A. A. Taylor. A suspension of coal in oil was cheaper than oil, had about 5 per cent. greater heat content per unit volume, and could lead to an increased use of coal amounting to about 750,000 tons per annum.

afloat. A fluid fuel may be made containing as much as 40 per cent. by weight of powdered coal, and mobile pastes containing up to about 75 per cent. Mobile gels may be made from either liquid or paste.

Ordinarily between 0.5 and 1.5 per cent. of rosin or a saponifiable oil is used, and 0.1 per cent. exercises a noticeable effect. The amount is determined by the nature of the mixture and the degrees of permanence desired. The bulk of the particles does not begin to settle until the period of "life" has passed, the colloidal fuel having a limited "life" which may be regulated to meet requirements—days for power plants, weeks and months for central storage stations and ocean-going vessels. Heat and agitation revivify the liquid fuel; the paste form may be kept for years.

"Colloidal" fuel is heavier than oil or water and saves storage space by compressing a maximum thermal value per unit of space. It may be stored under water to avoid evaporation, deterioration and fire risks. When sprayed into the hot fire-box, its oil-soaked solid particles are still further atomized by the sudden gasification of their imbibed oil. It possesses the advantages of fuel oil over coal in absence of smoke, dust and ash, practical elimination of labor in firing and filling storage space, thus saving time in "coal-ing" and in raising steam. The fire is likewise subject to instant control, and in naval operations a smoke screen may be readily produced by overfiring.

Another well-known colloidal fuel is "solidified alcohol," an alcogel usually stabilized by an alcohol soluble protector. Thus the late Prof. Charles Baskerville (College of the City of N. Y.) found that certain percentages of calcium acetate yielded with alcohol an unstable gel, which is stabilized by stearic acid.

## PETROLEUM

Colloidal phenomena are very marked in mineral oils. Many oils contain colloiddally dispersed water which is difficult to remove. The solid constituents of petroleum, especially the waxes, are largely in colloidal dispersion, some apparently serving as protectors to the others.\* This phenomenon is common, being found in alloys, glasses, mixtures of waxes, fatty acids etc. When the

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\* See *e. g.*, H. V. Dodd, Chem. Met. Eng., 1923, 28, 249.



kerosene and lower boiling fractions are removed from such oils, the solids, on chilling with ice, often assume the form of a gel which may be broken up by stirring or shaking, somewhat like agar gel.

Certain California petroleum was so viscous (Kern River field), that it could not be pumped through pipes, because the oil wet the iron and clung to it. To overcome this difficulty, Buckner Speed devised pipes with rifled bore, which gave the fluids passing through a rotatory motion. By pumping water and oil mixed together, the centrifugal force developed by the rotation caused the water to move to the outside of the pipe where it offered but slight frictional resistance, while the oil twisted through the center easily because it could not wet the water. Upon arrival at the end of the pipe line, the oil-water mixture readily separated, since there was no intimate emulsification.

Quite another situation, however, developed at another oil field, where a very fine emulsion of oil and water could not be "broken" even by steaming. Mr. Speed informs me that the water droplets were encased in extremely thin films, and the uniformity of the particle size indicated old geological origin. This recalls Trinidad asphalt (see p. 226). Cottrell and Speed found that with alternating current (Cottrell's precipitation uses direct current), if there was maintained a potential of about 10,000 volts per inch of electrode separation, and proper slow movement of oil provided, the water particles began a violent dance, and visible (on paraffin slabs) interchange of charges, and coalescence into large easily visible drops, which readily separated out by gravity. With lower potential gradient (say, 2,000 to 4,000 volts) per inch of electrode separation, the water particles built conductive chains between the electrodes (somewhat as iron filings between the poles of a magnet), and these chains conducted so much electrical energy, that the efficiency of the process was low. On the other hand, with potentials much above 10,000 volts, there was disruptive breakdown, with fire and smoke.

Mr. Speed writes me that "a very pretty test for a petroleum requiring electrical dehydration (or better, de-emulsification) is to make a solution of light (86°) gasoline with an equal amount of alcohol. They mix to a clear liquid. Then add one drop of the suspected petroleum, and, after shaking, one cc. of water. The alcohol and the gasoline separate, and on the brilliant meniscus

separating them there will be found floating the 'empty sausage casings' if the oil is a bad emulsion needing electrical treatment."

*Bloom* in oil seems to be in part caused by some colloidal constituent.

As Brooks and Humphrey have shown [J. Am. Chem. Soc., 1920, 40, 882], the "acid tar" which forms when petroleum is refined with sulphuric acid represents the coagulation of a previously existing colloidal dispersion of asphaltic bodies and the like, and not a polymerization product of olefines. Even 100 per cent. acid at 15 deg. C. does not produce tars from pure olefines. In some cases impurities may be centrifuged out, but they are largely removed by adsorption with fuller's earth, floridin, specially acid-treated bentonite, bauxite or other adsorbents. Patrick's colloidal silica gel and activated carbons are now used to adsorb the petroleum dispersed in natural gas, which yields millions of gallons annually of the high-grade "casing head" gasoline.

Great care must be used in drilling oil wells, for if the oil sands below ground get *wet* with water, surface tension makes the sand repel the oil, which is then unable to diffuse toward the well-pipe. Once the sands are *oiled*, however, then water cannot wet them.

In the drilling of oil wells, especially deep wells, "mud" is used to float up the core material, to prevent osmotic infiltration of salts, to counterbalance gas-pressure and obviate blowouts, etc. The chemical and physical conditions of the mud must be carefully controlled. Thus, bentonite is used to increase viscosity; barytes, and iron oxide to increase specific gravity; salts, to create osmotic counterpressure to salts in the various strata that may be met. On the other hand, the consistency must be so maintained that flow of comminuted material up the drill-hole will be sufficient. There must be a nice balance between thickeners, coagulators, deflocculators, etc.

In the rejuvenation of oil wells by gas pressure generated by the action of acid dropped down upon underground carbonates, it became necessary to protect the steel pipes against corrosion by the acid (generally HCl). This has been accomplished by substances which are powerfully adsorbed by the steel. Thus Mann, Lauer and Hultin (Ind. Eng. Chem., 1936, 28, 1048) find that aromatic amines, *e.g.*, aniline,  $\alpha$ -naphthylamine, form salts with the corroding acids, which, on ionization, form *inhibitor*

*ions* that form a protecting layer following their adsorption by the cathodic metallic areas.

In oil shale the oil is so finely dispersed that it cannot be removed by mere pressure. Distillation is resorted to, though doubtful claims are made that grinding in the colloid mill will effect a separation.

### ASPHALT

Although most of the mineral matter in asphalt exceeds colloidal dimensions, as Clifford Richardson has shown, the great extension of free surface caused by its presence adds considerably to the viscosity, strength and wearing properties of the asphalt. The minerals here function somewhat like the fillers in putties and lutes. Natural asphalts may be improved by the addition of colloidal clays.

Many years ago, H. Raschig, among others, patented the making of tar and asphalt emulsions by the use of water dispersions of clay. Later on Clifford Richardson found that colloidal clays, when used to emulsify asphalts or pitches, gave especially great strength and heat-resistance to the dried-out emulsion, and was granted patents for his discovery. Bentonite was among the colloidal clays used by Richardson, who used to exhibit two tubes containing spirals of the same asphalt, one with and the other without colloidal clay. The plain asphalt would melt and flow under temperatures which would not affect the asphalt reinforced with small percentages of colloidal clay, which, because of its great degree of subdivision and huge exposure of surface, produces effects out of proportion to its weight. These clay emulsions are useful because, while miscible with water and applicable to wet surfaces (roads, foundations, etc.), they become insoluble as they dry out, for they change from asphalt-in-water types of emulsions, to water-in-asphalt. The same relation exists between cream and butter.

Dr. J. S. Miller informs me that 5 per cent. of the mineral matter in native Trinidad Lake asphalt (the refined contains 36 per cent ash), is so fine that it will not settle from a 10 per cent. benzol solution on four years standing. About 80 per cent. of the mineral matter in the crude passes a 400 mesh screen. The constitution of asphalts is reflected in their ability to flow. Soft steam-refined asphalts appear to be truly viscous, but the hard

ones may show a yield point. Airblown asphalts also show structural viscosity, and many bitumen emulsions exhibit thixotropy (see p. 147).

L. Kirschbraun has patented the use of colloidal aqueous dispersions of asphalt, pitch, etc., which, when mixed with paper stock in the beater or on the way to the paper machine, may be flocculated out with alum or alum and sodium silicate, giving a highly waterproof and moisture-resisting paper. This asphalt dispersion is not sticky or adhesive under the conditions of pressure, etc., in the paper machine.

Among the many uses to which such emulsions are being put are protecting structural steel, patching roofs and highways, making waterproof cork insulation, pipe coverings, paints, building and roofing papers, auto body parts, and especially making a large variety of moisture and waterproof containers and wrappers for foods, tobacco, etc.

### "FIRE-FOAM"

"Fire-Foam" is a carbon dioxide froth made by mixing solutions of sodium bicarbonate and alum. A protective colloid such as liquorice, glue, dextrin, or saponin, is added to stabilize the foam and keep the bubbles in finely dispersed form. It kills fire by blanketing the blazing surfaces.

### INSECTICIDES

Petroleum oils are readily emulsified in water for killing San Jose scale and similar parasites, by the addition to them of sulphonated oils. Sulphur, Bordeaux mixture and the like are maintained in fine dispersion by colloidal protectors, as are also such poisons as lead arsenate. Minute quantities of poisons are sufficient to kill insects and it is wasteful to supply more than the necessary dose. The colloidal poison is less apt to be noticed and rejected by the insect and clings better to the plant, and goes much further.

Even allowing for the necessity of a rather promiscuous distribution of insecticides, in general the use of coarse particles means that the factor of safety is exceeded hundreds if not thousands of times; and this means enormous economic loss.

The electric charge of the dispersed insecticide is of importance. Since the leaves of plants are mostly negatively charged, positively charged colloids tend to cling closely to them, as has been pointed out by Dr. William Moore.

The various dispersing agents used with insecticides (*e.g.*, soap, casein) also act as "wetting agents," enabling the mixture to cling to the waxy leaf surface; and, later on, they may aid in washing off the poisons from fruit (*e.g.*, arsenic compounds from apples). Dilute sodium silicate has been recommended as a fruit detergent. (See H. C. MacLean and A. L. Weber, "Science," 1933, 78, 579.)

## CHAPTER XIII

### PRACTICAL APPLICATIONS (*Continued*)

#### FILTRATION

TO SECURE commercially successful filtration, a filtering medium or septum must be used, which, under the application of a practicable pressure, will permit the fluid to pass and still hold back the solids. The pores of the filter may initially be small enough, or they may become so by the deposit of some of the precipitate itself or of some added substance, such as paper pulp, shredded asbestos (Gooch crucible), or the like. Exceedingly dense filters may require the application of high pressure to force the fluid through, and such high-pressure filters were termed by Bechhold *ultrafilters* because they could be made to hold back ultramicroscopic particles. Bechhold ("Colloids in Biology and Medicine," translated by Dr. J. G. M. Bullowa) used gelatin jellies hardened in ice-cold formaldehyde, or a glacial acetic acid solution of collodion coagulated in water. These septa were supported on fine-meshed wire cloth to withstand the high pressure used.

With centrifuges and ultracentrifuges, as well as by sedimentation certain separations may be made without the use of a septum.

Zsigmondy has recently prepared *ultrafilters for analytical use*, which permit the rapid and successful filtration of troublesome precipitates [see Zsigmondy and Jander, *Zeit. anal. Chem.*, 1919, 58, 241].

The so-called *stream-line filter* of Hele-Shaw consists of paper sheets tightly pressed together, with holes bored through the pack at right angles to the surface. Liquids are forced under pressure into one set of holes and pass between the sheets to the adjoining set. By sufficient compression of the sheets, even Prussian blue may be filtered out of solution.

Anything that favors deflocculation of a precipitate or the formation of a fine or colloidal precipitate, such as protective colloids, dilute alkalis, and so on, works against clear filtration.

Thus Zsigmondy found that a gold hydrosol, whose particles were 20 to 30 millimicrons, passed freely through Pukall and Maassen filters if egg albumen was present. In the absence of the protective albumen, the colloidal gold was adsorbed by the filters, gradually clogging their pores until the filtrate, at first red, became colorless. (See pp. 126 and 127.)

In technical practice, wherever possible, a coagulated precipitate is formed whose large particles are held back with comparative ease. Therefore, glucose liquors, for example, must be acid to filter well. Where protective colloids interfere with filtration, their protective action may be destroyed by coagulation, hydrolysis and the like. *Filter aids*, which tend to adsorb colloid particles, are in extensive use; *e.g.*, paper pulp, diatomaceous earths.

### SEWAGE DISPOSAL

Sewage usually contains considerable amounts of deflocculating substances, such as soap, organic matter and the like, which tend to keep it full of colloiddally dispersed particles. The successful treatment of sewage, backwaters, and trade effluents involves the separation from them of these colloids by coagulation, adsorption, filtration, or destruction (usually by bacteria in the septic tank). The old "ABC" method depended on the use of alum, blood, and clay (whence the name) to make a coagulum that would carry down suspended matter. Ferrous sulphate and lime (yielding a coagulum of ferric hydroxide) and alum are also used as clarifiers and coagulants. H. M. Spencer (Chem. Age, Jan. 1924) uses a colloidal solution of aluminum hydroxide, which on dilution forms a gel.

In the *activated sludge process* it has long been known that the effective acidity of the sewage controls proper settling, and modern methods of  $p_H$  control aid in fixing the isoelectric point, most favorable to flocculation. See paper by Prof. A. M. Buswell (University of Illinois) on "Colloidal Aspects of Waste Treatment," in Alexander's Colloid Chemistry, Vol. IV, pp. 669-95.

Filtration through sand, coke, and the like serves to adsorb colloidal impurities, but filters of this kind do not begin to function properly until they become coated with a gel-like slime containing many bacteria. There has been much discussion as to whether the action of the filter depends on activity of the bacteria

in destroying and dispersing to the crystalloidal state the finely suspended or colloidal matter, or whether the removal of these substances is not an adsorption phenomenon due to the extended surface of the filter bed. Both effects exist, the latter being the more important, and depending largely on the action of the bacterial jelly that forms the surface layer.

## PHOTOGRAPHY

The ordinary precipitate of silver bromide obtained by mixing equivalent amounts of potassium bromide and silver nitrate is flocculent and quickly settles. If the fresh precipitate (before or after washing) is shaken with a solution of gelatin containing a trace of potassium bromide, or better, yet, if the precipitate is originally formed in the presence of gelatin, there results a colloidal solution of silver bromide, which may be exceedingly fine or grainless, depending on conditions. The latter method is used mainly in preparing photographic "emulsions."

The Lippmann "grainless" emulsion is an illustration of the principle of *plural protection* discovered by J. Alexander [J. Chem. Ind. Eng., 1923, 15, 283], for in preparing it gelatin is added to both the silver nitrate and the bromide solutions before they are mixed (see p. 156).

As a very fine emulsion is relatively insensitive, it is "ripened" by allowing the silver bromide grains to grow until they are about 0.4 to 10 microns in diameter, the process being facilitated by heat. Certain percentages of chloride and iodide may be used, a small excess of the soluble halide salt aiding in peptizing or stabilizing the precipitate, and keeping its particles within the desired limits which are about 2 to 3 microns in most cases.\*

When a sensitive ripened emulsion is exposed to light, some of the silver halide is decomposed, its halogen being probably held by the gelatin,† while the metallic silver forms a colloidal dispersion in the rest of the silver halide, yielding the so-called "photo-halides." These were long supposed to be subhalides (sub-bromide and so on) of silver, but are now recognized as be-

\* According to Lottermoser the excess of soluble halide gives the particles of silver halide a positive charge, essential to their sensitivity to light.

† Chlorine, bromine and iodine all "tan gelatin"; see Allen's Commercial Organic Analysis, 5th ed., vol. 10, article on Albuminoids or Scleroproteins; also A. C. S. Monograph No. 11, "Glue and Gelatin," by J. Alexander.



ing of the same nature as the "metal fogs" which often appear during the electrolysis of molten salts, and consist of colloiddally dispersed metal.

Recently, Dr. S. E. Sheppard and his collaborators at the Eastman Kodak Company have shown the importance of traces of impurities in gelatin in forming silver sulphide nuclei, which make the plate or film highly sensitive. They believe that the active material consists of traces of thiocyanates derived from "mustard oils" in the fodder of the cattle from whose skins and bones the gelatin was made. It is said that similar facts were long known to A. and L. Lumière in France, but kept as a trade secret.

The particles of silver in the "latent image" are so exceedingly fine that, in time, they apparently recombine again with the halogen, and the latent image fades away. To render it permanent, it must be treated with a "developer," a reducing agent which probably serves the twofold purpose of combining with the halogen and making the extremely fine silver grow into dense visible particles or grains.

The color of emulsions varies greatly with the size of their "grains." Fine blue emulsions are sensitive to red, and even to infra-red rays. Freshly prepared emulsions appear red to transmitted light, but on ripening the color changes to green, the particles increasing from below 0.1 micron to over 0.5 micron. The photo-halides resulting from the action of light on emulsions are also highly colored.

### BREWING

In the brewing process it is essential that the starch originally present be converted into sugars which can be fermented, or into very soluble dextrans. In fact both the albumin and the dextrin in beer must be finely enough dispersed to remain clear in solution. Many factors in the brewing process may tend to coagulate the albumin. The influence of solid surfaces is seen by changing the inner lining of the fermenting vessel. A certain wort, which showed 0.2450 per cent. of albumin when fermented in a glass or enameled vessel, showed only 0.1925 per cent. in a paraffin-lined vessel, and 0.1750 per cent. in one lined with pitch.

Old-fashioned brew-masters would never use any vessel unless it had first been treated with a decoction of malt kernels and nut leaves, or else with "*fassgeläger*" (barrel dregs) which

acts like the so-called "*bierstein*," a deposit mainly of organic substances that forms on new surfaces, and prevents them from coagulating albumin.

Fluid surfaces also exercise an effect as may be seen from the fact that in the chemical analysis of beer, such substances as benzol, chloroform and benzin are used to coagulate and shake out the beer colloids.

Gas surfaces are also active. Their formation tends to coagulate the dissolved albumin, and this fact killed the so-called "vacuum fermentation process" designed to recover and use the carbon dioxide liberated on fermentation. Jarring due to transportation or passing railroad trains may have a deleterious effect. A slight trace of acid tends to stabilize the albumin, as do also the tannin and resin from the hops, the dextrins from the mash, and the inorganic colloids of calcium and magnesium. The excellent brewing qualities of the water of the River Trent (England) are in large measure due to the lime content of the water, and patents have been taken out for "Burtonizing" water by the addition of lime salts.

To secure the formation of a lasting foam and a desirable "body" (*Vollmündigkeit*), a proper balance is necessary between dextrin and albumin. Where beer is served icy cold, the chilling produces cloudiness because of the aggregation or partial coagulation of the albumin. This was cleverly overcome by Wallerstein, who introduced into the beer a proteolytic enzyme (pepsin or papain) which, by increasing the dispersion of the albumin, prevents clouding.

Isinglass and gelatin are largely used for fining beer and astringent wines. A solution of the fining agent is poured in through the bung and settles down through the cask as a gel which effectually entraps all turbidity-producing particles. The tannin present aids in coagulating the gelatin or isinglass.

## TANNING

The object of tanning is to make the hide or skin resistant to water, wear, and bacterial attack, at the same time giving it tensile strength, pliability, and capacity to maintain, when dry, a shape given it when wet, which somewhat resembles a permanent set in metals.

The skins or hides of animals consist of an organized colloidal jelly, formed of bundles of fine fibrils about one micron in diameter, bound together by cementing substance of similar chemical composition which is largely removed by liming and other treatment preceding the tannage proper. The principal protein of the hide is called collagen (*glue-former*) since from it gelatin and glue may be produced by heating with water. The old processes of bateing, drenching, puering, etc., tended to neutralize the lime and bring the collagen into a flaccid or unswollen condition; in addition, the bacterial enzymes digest off part of the remaining cementing and epidermal substances (elastin) and complete the emulsification of the fat. Synthetic mixtures consisting mainly of ammonium chloride and tryptic ferments (pancreatin) are now largely used in place of the foul-smelling bacterial baths which often ate off the grain of the skin.

The work of Dr. Max Bergmann (Science, 1934, 79, 439-45) indicates that when a dipeptase attacks the peptide linkage of a dipeptide, "the enzyme may be . . . regarded as combining chemically with at least three different atomic groups of the dipeptide, that is to say with the carboxyl ( $\text{COOH}$ ), the amino group ( $\text{NH}_2$ ) and the peptide linkage ( $\text{.CO-NH.}$ ). The presence of hydrogen atoms in the  $\alpha$  and  $\alpha'$ -positions, and in correct spatial configuration, is also essential." This confirms Emil Fischer's lock-and-key relation between enzyme and substrate. Tanning masks some of these bonds essential to enzyme action, and this may be one reason why bacteria do not attack leather readily. On the other hand, when leather is wet, some tannin "bleeds out" and may adversely affect bacteria. Tannin-containing woods, *e.g.*, chestnut and oak are relatively resistant to bacteria and moulds.

The collagen fibrils, which are about  $1\mu$  in diameter, are composed of bundles of long polypeptide chains, held together sideways by secondary valence forces which are weaker than the end-to-end forces uniting the amino acid molecules into chains. Prior to tanning, the hide is "opened up" by treatment with mild alkaline solutions, usually lime water, so that the fibrils comprising the fibers separate sufficiently to permit diffusional entrance of the tanning material. The tannins then combine with reactive side-chains in the long peptide molecules and perhaps also with the imino linkages of the main chains. This diminishes their

water-attracting capacity, although some water is taken up in the grosser capillary structure.

The amount of tannins fixed by the hide (that is, the poundage yield) is governed largely by the extent to which the hide is "opened up." Too great a disturbance of the sidewise bonds weakens the leather. The tanner's practical experience determines the degree of treatment for various and variable hides and skins, needed to produce leathers of widely differing properties suited for different uses—shoe-soles, gloves, pump-washers, clothing, etc.

In vegetable tannage, the prepared hide is placed in an acid tannin solution (tan liquor), whereupon the hide powerfully adsorbs tannin and combines with it to form leather. In alkaline solution both tannin and hide are negatively charged, and no tanning occurs; in fact, leather may be stripped of tannin by alkalis. It is still a moot question whether the combination is chemical or physical, but since the fixation follows an adsorption isotherm and is very variable in percentage, it may be justly termed a colloid combination which partakes of the nature of both. The positively charged hide and the negatively charged tannin mutually coagulate each other. Neutral gelatin, if practically free from electrolytes, does not precipitate pure tannin, but in acid solution it takes a positive charge and is tanned. The tanning process may be aided by giving the hide a suitable electrical potential, positive in the case of vegetable tannage, negative with chrome.

To prevent the skin from being "case-hardened" by too rapid a deposition of tannin, which would make it act as an ultrafilter and prevent proper tannage of the interior layers, the tanning is commenced in very weak or spent liquors, and the skins are moved to baths of progressively increasing strength (counter-current method). This is the tanner's "Golden Rule."

Non-tannins seem to play the rôle of protectors to the tannins, and the general rule is that tanning liquors having the highest tanning/non-tannin ratio are the most astringent. The degree of dispersion thus appears to be an important factor; for if properly dispersed, tannin easily enters the tiny interspaces between the fibrils. The efficiency of certain synthetic tanning agents used preliminary to heavy vegetable tannage may be consequent to their protective action, or to their ability to enter into close

combination with the charged "centers" in the long peptide chains, leaving the presumably larger tannin particles to combine with the side-chains. [See J. Alexander, "Degree of Dispersion as an Influence in Tanning," J. Am. Leather Chem. Assn., 1923, Vol. 18, 400.]

The degree of dispersion of the tannin and the incidental impurities present also influence the intimacy with which the tannin is fixed by the hide. By extraction with organic solvents G. Powarnin (Collegium, 1923, 222-228) obtained the following results from a quebracho tanned leather which showed a cold water extract of 9.54 per cent. by the Koch-Procter method: water-soluble material removed upon Soxhlet extraction by acetone, 12.5 per cent.; by ethyl alcohol, 17.2 per cent.; by methyl alcohol, 22.2 per cent. His tabulated results indicate that for every different tanning material used, part combines chemically and part is adsorbed.

Prof. E. Stiasny (Technische Hochschule, Darmstadt), after commenting on the uncertain chemical composition of vegetable tanning materials, states: (Alexander's Colloid Chemistry, Vol. IV, p. 431): "The tanning properties, the astringency, the speed of diffusion, the degree of adsorption and the reversibility of adsorption (ease of washing out of the tannin) are properties depending more on the degree of dispersion and other colloid properties than on the chemical constitution." Dr. D. Jordan Lloyd (9th Int. Cong. Pure and Appl. Chem., Madrid, 1934; Trans. Faraday Soc., 1935, 31, 317-24) points out that smaller tannin "molecules," because of their greater kinetic activity, are more apt to jiggle off than a less active, larger particle; and the latter is, furthermore, attached by many more bonds. She and her collaborators also found that tannin solutions with larger particles are more astringent. It would seem, therefore, that there is a *zone* of optimum dispersion, the tanner's "Golden Rule" above referred to being "only a special case of the general principle that high dispersion is necessary at the commencement of tannage and that as tannage proceeds the dispersion should gradually become lower." (Stiasny, *loc. cit.*). Neither gallic acid nor catechol is a tanning agent; but their condensation products, pyrogallol and catechin, will tan. Condensation increases molecular size and slows down Brownian motion. See p. 36, on the zone of maximum colloidalilty.



others, thinks that a definite chemical combination occurs subsequently. The whole process, however, seems to be a hydrolytic splitting of the salts, accompanied by adsorption (or *sorption*, to use McBain's non-committal expression), of the insoluble basic metallic salt by the hide fiber. The increasing stability of alum-tanned leather upon ageing would, then, be due to colloidal synthesis. Gelatin heated for a while at 120° becomes insoluble.

*Fat tannage*, which yields chamois, buckskin, washleather, and the like, is effected by introducing oxidizable oils, usually in the form of a colloidal emulsion, into the skin. The view that fat tannage is due to aldehydes, developed by oxidization of the glycerin in the fats used, seems negatived by the fact that free fatty acids themselves may serve as tanning agents. Apparently the colloidal fat and the hide, being oppositely charged, form an adsorption compound. Knapp made a fair grade of leather by simply soaking a flaccid skin in an alcoholic solution of stearic acid.

## PAPER

The first paper maker was the hornet or wasp, who, by chewing up wood in the presence of his colloidal salivary secretion, imitated on a small scale the action of the "colloid mill." There is no doubt that the prolonged and thorough grinding that paper stock gets in the beater, besides bringing much of it to a swollen or gel-like state, reduces part at least to a colloidal condition. This colloidal cellulose evidently exerts a powerful cementing action, far above what would be indicated by the small percentage present by weight, resembling in this respect the "ultra-clay" which exerts so great an effect in soils. The formation of a coherent web on the Fourdrinier wires thus depends on the greatly extended free surface of the "stuff" or paper stock, and perhaps the addition of a little colloidal cellulose will materially shorten the time in the beater. "Glassine" papers are produced by excessive beating.

In *engine sizing* a colloidal emulsion of rosin in rosin soap is generally added to the beater pulp, and, after being thoroughly mixed in, is precipitated by adding alum or aluminium sulphate. The colloidal rosin and the alumina gel help bind the paper fibers together and to make the paper stronger and resistant to water. Many substitutes for rosin have been used (silicate of soda, glue,

and so on) which are added in colloidal solution and subsequently precipitated. To prevent the glue from being largely lost in the back waters, some highly adsorbent filler such as talc or clay must be added to the pulp to adsorb and hold the glue.

*Tub sizing* of paper involves passing the finished web through a bath of some such colloidal solution as gelatin, glue, starch, and the like, which, on drying, fills the pores and prevents ink from spreading or "bleeding," besides adding to the finish, strength and "handle" of the paper. The nice, crisp crackle of new banknotes and of stocks and bonds is due to a bath of alum and glue.

Bibulous papers, such as *blotting paper* and *filter paper*, are made without sizing, reliance being placed for their strength on the binding properties of the colloidal cellulose. Recently rubber latex has been used as a paper size.

The speed and the degree of drying paper are also factors materially affecting its strength.

*Colloidal clays* have found several uses in the paper industry. They tend to improve the luster of friction coated papers. Asphalts or tars may be emulsified with water by their aid, and incorporated with the paper pulp in the beater, thus serving both to size and to waterproof the paper. In using resinous woods, the resin often accumulates into small masses or "balls" which stick on the Fourdrinier wire, and cause holes, tears and shut-downs. The addition of colloidal clay to the beater converts the resin into a non-coherent emulsion by coating over the resin particles, and thus eliminates the damage. Old newspapers and magazines may be de-inked by beating and macerating them with a little alkali and colloidal clay, which adsorbs the loosened ink so that the two may be washed away through a special screen. It is estimated that a ton of good standard newspaper can be produced from a ton and a quarter of old newspapers, and by gathering the waste in big cities alone there would be possible an annual saving equal to the cut on 275,000 acres of thickly wooded spruce forest. (Forest Products Laboratory, Madison, Wis.)

## RUBBER

The milky juice (*latex*) of several kinds of plants yields on coagulation the colloidal gel called rubber. The latices are emulsions containing rubber and resin, stabilized by protective



colloids (proteins or peptones) and the kind of coagulant used depends on the nature of the protector. Thus formaldehyde preserves latices whose protectors are proteins, but coagulates *Kickxia* latex by precipitating the protective peptones.

*Vulcanization* consists in the combination of sulphur with rubber. The sulphur is at first adsorbed, and upon heating enters into a very close combination with the rubber, which is generally believed to be a true chemical combination, though it may incidentally catalyze intramolecular rearrangement or double linkages.

*Fillers* increase considerably the strength and wearing power of rubber (in automobile tires, for example) by greatly extending the free internal surface. The rôle of fillers in rubber is similar to what it is in putty, and is therefore intimately bound up with their degree of dispersion. Carbon black, zinc oxide and magnesia are valued in the order given, which represents the relative order of fineness of their particles. Especially fine fillers have recently been produced which are said to give the tread of automobile tires a much longer life than those made with ordinary products.

Scientific research, largely in the colloidal field, has reduced the mileage cost on automobile tires to about one-tenth of what it used to be. Not only are tires about one-third lighter in weight, but their "road life" has risen from an expectancy of about 3,000 miles to 15,000 miles. The use of *accelerators* in vulcanization has greatly increased the output per unit of manufacturing plant, avoiding the need of further huge capital investment in fixed form. Anti-oxidants also aid tire life. The native-cured "wild" rubber used to contain nitrogenous impurities which facilitated the "cure" (vulcanization); but with the purer "plantation" rubber, accelerators were all the more needed.

Patents have been taken out for incorporating colloidal precipitates in rubber, and even glue jelly is worked into tires to improve their wear by increasing the interior free surface.

*Rubber latex* is now being largely imported and used for directly impregnating fabrics which are then vulcanized, and also for adding to paper pulp in the beater. Tough, waterproof paper may be thus made.

Wm. B. Pratt patented a process for dispersing commercial rubber (coagulated latex) in water (Italian Pat. 225,949, Dec.

12, 1923). Believing that the original globules in latex maintain their identity after coagulation and even after vulcanization, he incorporated protective colloids (soaps, glue) with the rubber, or formed them *in situ*, and then gradually worked in water. The rubber may first be swollen with benzol to open it up. As the coagulation of rubber was thought to be irreversible, this is practically unscrambling an egg. (See J. B. Tuttle, *India Rubber World*, Jan. 1924; *Chem. Met. Eng.*, March 10, 1924.)

Mixtures containing rubber latex or re-formed rubber dispersions are largely used as adhesives. Chlorinated rubber is a derivative product which is finding use in lacquers, paints, moulding compounds, etc.

#### PLASTICS—RESINS, SYNTHETIC AND NATURAL

At a meeting of the American Chemical Society held on Feb. 5th, 1909 at the original home of the Chemists' Club in West 55th St., New York City, Dr. Leo H. Baekeland (Columbia University) first exhibited his "Bakelite" discovered about three years previously (*Ind. Eng. Chem.*, 1909, 1, 149-61). Though all of us present were greatly impressed by his samples and demonstrations (*e.g.*, he boiled a treated hair-brush back for some time without affecting its brilliant gloss), and while all recognized his work as a major achievement, no one could have foreseen the immense scope of the modern plastics industry which there had its beginning.

The behavior and properties of "Bakelite" indicated its colloidal nature. Starting with about equal parts of phenol and formaldehyde containing a small amount of alkaline condensing agent, Baekeland classified the products emerging into three groups: *Initial condensation product A*, which may be liquid, viscous, pasty, or solid, but dissolves in a variety of solvents; *intermediate condensation product B*, insoluble, though it swells in solvents, and becomes rubber-like when heated but does not melt; *final condensation product C*, insoluble and infusible. This seems to justify the view of Dr. H. L. Bender (*Alexander's Colloid Chemistry*, Vol. IV, p. 361) that the first two processes may be regarded as chemical condensation and polymerization, the final process being in the nature of a physiochemical coagulation. That is, molecules formed by chemical interaction of the phenolic

substance used with the formaldehyde, polymerize \* to form giant or *macromolecules*, and then these aggregate to make the final product.

In the effort to unravel the chemical tangles involved in the formation of "high-molecular compounds," appreciation of the colloidal aspects only slowly emerged. Staudinger ("Die hoch-molekularen organischen Verbindungen," J. Springer, 1932) grouped them in order of increasing molecular size and complexity into *hemicolloids*, *mesocolloids*, and *eu colloids*, which is interesting in connection with the concept of the zone of maximum colloidalilty (see p. 36). Recently (Trans. Faraday Soc., 1936, 32, 97), on the basis of viscosity measurements, Staudinger distinguished between linear and sphero types of aggregation. In view of what has been found in connection with proteins and carbohydrates (see pp. 294 and 306), and the possibilities of colloidal protection and the effects of "impurities," it is evident that a wide variety of effects may be produced by differences in raw materials and manipulation.

Under the stimulus of Baekeland's pioneer discovery, many other kinds of synthetic resins and allied plastic materials were developed. In an appendix to his valuable book "The Chemistry of Synthetic Resins," (Reinhold Pub. Co., 1935), Dr. Carleton Ellis tabulates about 1,100 commercial names of such products, with particulars about them. Recent papers presented at special Symposia before the American Chemical Society (Pittsburgh, 1936) and the Society of Chemical Industry (London and Liverpool, 1936) will be found in their respective journals. References to the immense literature will be found in Ellis' book and in the indexes of many chemical publications. Interesting in this connection is the paper of P. P. von. Weimarn "On the Rubber-like and Liquid-crystalline States of Matter, in Connection with the Classification of Crystals and Molecules According to their Vectorial Fields" (Alexander's Colloid Chemistry, Vol. III, pp. 89-102).

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\* Polymerization" should be restricted to cases where the final product is a multiple of the initial molecule. Thus paraldehyde (used as an hypnotic) is a *trimer* of acetaldehyde ( $\text{CH}_3\text{CHO}$ )<sub>3</sub>; it is readily broken down again, which is not the case with the polymer formed when a phenyl is first substituted in the methyl group. However, the terms *polymerisation* and *condensation* are loosely used so as to include a wide range of changes whereby more complicated products are formed. See *e.g.*, Ellis, *lib. cit.*, Vol. I, p. 42.

Paul J. Flory states (J. Am. Chem. Soc., 1936, 58, 1877):  
“All synthetic polymers and most natural ones are recognized to be non-homogeneous substances consisting of mixtures of chemically similar molecules which are distributed in size about an average, some of them being much smaller and some much larger than this average.”

## CHAPTER XIV

### PRACTICAL APPLICATIONS (*Continued*)

#### FOODS AND THEIR PREPARATION

IT is a serious error to judge foods on the basis of a bald chemical or calorific analysis. Fat, protein, carbohydrate and calories alone are not fair criteria of food value; the physical condition of the food and the presence of certain "impurities" now recognized as essential (for example, vitamins) largely affect the usefulness of a food to the organism. The experience of centuries has taught us the value of cooking which hydrolyzes, swells up, or softens many foods and usually destroys the species-specificity of proteins. The Chinese sprout many grains before cooking them. "Light" bread or cake has been leavened by yeast or baking powder until it presents an enormous surface to the digestive juices; as we learn from the Bible, unleavened bread was eaten only in times of stress. Egg-albumen, when cooked, is more slowly absorbed and its coagulum is reduced to its constituent amino-acids which are absorbed as such. Therefore, some persons who have an idiosyncrasy against raw eggs (possibly because of a permeable or ulcerated stomach wall) can eat cooked eggs.

The meats yielded by young animals are more juicy and tender than those obtained from older animals, because the latter consist of tissues which age has hardened by syneresis and dehydration. In cooking meats, the exterior is seared to retain the juices (*e.g.*, pot roast); but in cooking soup it is simmered to extract them. Many foods are highly emulsified (cream and mayonnaise, for example), and this permits their more ready assimilation. Cream is a natural emulsion of fat in water and *wets* blotting paper; butter is an emulsion of water in fat and *greases* paper. The presence of protective colloids in foods containing milk (ice creams, Bavarian creams and the like) is an aid to their digestibility.

The ancient art of cooking, however, involves psychological factors besides mere digestibility and ease of assimilation; taste, flavor, odor and variety are important. An old Southern saying is: "The Lord sends the victuals, but the Devil sends the cooks."

From time immemorial many colloid chemical principles have been utilized in the kitchen; *e.g.*, the making of Hollandaise sauce, mayonnaise, clarifying coffee by adding egg shells containing some adherent albumen, salting water to "set" eggs in poaching. Agar, an indigestible carbohydrate, forms a hydrous residue stimulating to the intestines.

In making coffee, the water must be heated hot enough to expel the gases adsorbed in the capillary spaces of the roasted bean, and permit the water to enter and dissolve out the caffeine and other solutes. The escaping gases form a temporary froth on top of the coffee. Cooks call this bringing the coffee "to the cream."

Many cooks (in France, Belgium, Louisiana) use a small amount of roasted chicory root in coffee. The quantity is too small to mean adulteration, and it is used even when coffee is cheaper than chicory. Experiments indicated that chicory, in minimal amount, improved color and "body," besides helping to prevent the escape of the "oil" which gives the coffee its characteristic aroma, a matter of importance where the coffee is not used immediately but stands for a while. Color, odor, and "body" are what most people seek in coffee; the stimulating caffeine is generally present in ample sufficiency—in fact, many use coffee from which the caffeine has been extracted. The dark color generally demanded can, with the aid of chicory, be had with medium roasted coffee, without recourse to high roasted coffee which contains empyreumatic substances. This is no plea for the use of chicory, but simply an attempt to understand why some cooks use it.

Oysters, scallops, etc., are often allowed to "drink" fresh or brackish water, which removes repressing salts and permits swelling or plumping. Besides the danger of bacterial contamination, it was found that ten gallons of scallops were swollen to 17 gallons, with no increase in food value. The process is sometimes called "fattening."

In making "cream of tomato," it is usual to add some baking soda (bicarbonate) to prevent the acid fruit from coagulat-

ing the milk or cream. (But the alkali may effect the vitamins present.)

Following the *somatic death* of an animal (death of the organism as a whole), the blood-stream ceases to flow and to bring in oxygen and remove carbon dioxide. The still living cells are killed by lack of oxygen and by the accumulation of materials of their own metabolism, mainly lactic and carbonic acids, the former an intermediate in the oxidation of dextrose, the fuel sugar of the blood. That is, *cellular death* is accompanied by a change from a feeble alkalinity in most of the body, to an acidity which is mainly responsible for *rigor mortis*, a stiffness which gradually disappears as the initial coagulative reaction is followed by lysis.

These lytic effects are responsible for the fact that meats become more tender on "hanging" or ageing. The softening may reach an extreme in "high" game, and is often aided by vinegar (*e.g.*, in marinated meat or herring, "soused" mackerel, etc.).

In considering the preservation of white fish, Geo. A. Reay (Torry Research Station, Aberdeen) found (J. Soc. Chem. Ind., 1935, 54, 145-8) that *quality* involves appearance, structure, texture and palatability. With iced fish, after *rigor mortis* passes off, the flesh softens, blanches, and becomes less translucent in about 7 days. If 40-100% CO<sub>2</sub> be present, the flesh blanches in about 3 days, and becomes more crumbly than in simply iced fish of same age. "This is probably a pH effect, due to carbon dioxide dissolving in the muscle, and causing a shift towards the isoelectric region of the proteins, diminishing their hydration and increasing their susceptibility to denaturation." Freezing below -6° C. while it stops bacterial development, results in extensive blanching and friability, and to "drip" formation (syneresis) within a week, "quality" suffering. "This type of colloidal change affects palatability through rendering the flesh dry or 'wooly' on the tongue," and is quite noticeable in cod and haddock in CO<sub>2</sub> and in frozen fish but not in iced fish. It is bad for smoke-curing, and is associated with diminished peptisability of muscle myosin in neutral salt solutions. Prior to smoke cure, the fish are dipped in solutions of NaCl, 20% or stronger, which should peptise the superficial myosin and give a shining pellicle or glaze; but fish frozen or stored in CO<sub>2</sub> will not give a good "glaze," and this militates against the better-preserved "frozen" fish because of the buyer's prejudice, based on appearance.

## BAKING

In China, 2000 B. C., the art of baking bread was already an ancient one, and probably developed from the observation that fermentation of the dough by wild yeasts improved the bread. Bread involves a rather complicated colloidal system consisting of starch, gluten, salts, yeast enzymes, and often fat and milk. That the system must contain stabilizing factors is indicated by the fact that almost anyone, working by rule-of-thumb methods, can produce a fair loaf.

Although the temperature of a bread oven usually runs between 200 deg. and 240 deg. C., the interior of the loaf seldom goes over 95 deg. C. Wheat starch is completely gelatinized at 65 deg. C. if sufficient water be present; but as the average dough holds only about 40 per cent. of water, a large part of which is taken up by the gluten, the baked loaf is full of starch granules that have been only partially swollen and gelatinized. According to R. Whymper ("The Conditions That Govern Staleness in Bread," Maclaren & Sons, Ltd., 1919), the gluten acts as a colloidal protector to the starch, maintaining its dispersion and water-holding capacity.

The *velocity* with which a loaf of bread is baked is a more important factor than is generally realized, for there must be a nice coordination between the time and thickness of "crusting" and the speed of "rise" of the loaf, if a satisfactory product is to be had. With too quick an oven, "skinning" is so rapid and tough that the loaf cannot rise properly and is "heavy." With too "slow" an oven, the skin or crust is too weak and the loaf "splits," or overflows. The same applies to baking cakes.

The gluten of wheat flour and like grains is itself a colloidal complex and of variable composition, containing glutenin, gliadin, globulin, albumin and so on in different proportions. The baking properties of flour, that is, its ability to hold water and the leavening bubbles of carbonic acid gas evolved by the yeast, depend mainly on the physical condition of its gluten. This in turn depends on the relative ratio of the several colloids, and especially on the presence of salts which materially affect their solubility and their protective relation to each other, as is evident from the following:



Gladin forms an opalescent colloidal solution in distilled water, from which it is precipitated by sodium chloride.

Glutenin is insoluble in water or saline solutions. It dissolves in dilute acids (or alkalis), and is thrown out again upon neutralization.

Globulin and albumin are soluble in sodium chloride solutions.

The various gluten fractions can hardly be said to be definite chemical individuals, and their purification, followed by an investigation of their mutual influence on each other, and also the influence of salts, constitutes a fruitful field for research. It is probable that we shall find here an instance of cumulative protection, where, for example, the protective action of the gliadin on the glutenin is enhanced by the protective action of the globulin and albumin on the gliadin. Salts, by changing the degree of dispersion or solubility of the several fractions, must shift the equilibrium of the complex system. So also does the slight acidity developed by the yeast. Thus, Weyland Bischoff (Jago, "The Technology of Bread-making") found that flour moistened with a 15 per cent. solution of sodium chloride yielded a dough deficient in tenacity. Flour heated for several hours at 60 deg. C. will not make a dough, probably because one (perhaps more) of its colloids has lost so much water that the constituent particles have approached too close to be separated by water alone. This is similar to the action of gelatin, which loses its solubility upon being heated at 110 deg. C. or above.

The best results with flours are obtained by using water containing small amounts of sodium chloride. Salt, used from time immemorial, besides adding to palatability, enables the gluten to absorb and hold water, an effect shared by chlorides generally. Hard waters, containing sulphates or the like, harden the gluten; whereas, soft alkaline waters disintegrate it and destroy its elasticity. Even distilled water yields a sticky dough.

H. Jørgensen found (Biochem. Z., 1935, 280, 1; 283, 134) that flour "improvers," *e.g.*, bromate, perborate, persulphate, oxidize and remove from action a natural *activator* normally present in flour, thereby decreasing the proteolytic enzyme attack on the proteins, which lowers their quality for bread production. This was confirmed by E. Waldschmidt-Leitz (Chemistry and Industry, 1936, 55, 624).

The importance of water in bread-making is obviously on a par with its importance in brewing, and in both cases the mineral impurities affect the yeast. Alum, calcium sulphate and even sulphate of copper have been used to improve gluten, especially in spoiled flours. Potassium bromate, recently introduced as a "yeast food," may also register its effect on the colloidal condition of the gluten.

While the carbon dioxide formed by the yeast is initially liberated in nearly colloidal dispersion, it soon forms visible bubbles, which, however, must be kept in fine dispersion by the elastic gluten if a loaf of good texture is expected. The addition of a little fat to the dough and the use of, say, half milk and half water, both serve not only to improve the texture of the loaf, but to add materially to its keeping properties. Whympers attributes the keeping properties of the home-made farm loaf to the protective action of fats on the starch—that is, fat tends to prevent *staling* of bread. The casein and salts of the milk also affect the gluten, and the milk fat or other added fat, by going into emulsion, tends to coat over the dough particles and prevent desiccation. Such action of the fat results in *shortening*, the resulting bread, cake or biscuit being flakier and more brittle.

In baking "light" cakes, it is usual to separate the yolks from the whites of the eggs, and to beat the whites to a fine froth before "folding" them into the batter (containing flour, milk, egg yolk, shortening, sugar, flavoring), thus introducing finely dispersed, leavening air bubbles. If the whites and the yolks are beaten together, the lipoid or fatty material in the yolks goes to the air/egg interface, giving bubbles which readily break. In the absence of fats, a stabilizing film of albumin forms at the air/egg-white interface. Similar practise is followed in making *soufflé* dishes, *e.g.*, omelette soufflée.

Where very "light" cake is desired, *e.g.*, sponge cake, no shortening (fat) is added to the batter, and angel cake is baked in paper to avoid greasing the bake pan.

The "roux" used by French cooks for thickening sauces, etc., is made by dispersing flour in fat (generally butter). A *roux* mixes readily with hot water or milk, and on boiling yields a smooth creamy emulsion as the starch grains are gelatinized. The fluids should be added a little at a time, with constant stirring.

## MILK

From a colloid chemical standpoint, the main constituents of milk may be classified as follows:

In crystalloid dispersion:

Salts (*e.g.*, NaCl).

Sugar (lactose).

In colloidal dispersion:

Casein, an unstable or irreversible colloid.

Lactalbumin, a stable, reversible, protective colloid.

In suspension or emulsion: Milk fat.\*

Most formulas and recipes for modifying cows' milk for infant feeding and almost all analyses of milk combine the percentages of casein and lactalbumin under the collective title of "total proteids" (in modern form, "total protein"; globulin is also included), thereby obscuring the highly important fact that the lactalbumin stabilizes and protects the casein from coagulation by acid and rennin.

The subjoined table, giving average compositions in per cent., shows how natural milks are influenced by variations in the casein/lactalbumin ratio:

TABLE XIX

Kind of milk.	Casein.	Lact-al-bumin.	Pro- tec- tive Ratio.	Fat.	Behavior with acid and rennin.
Cow.....	3.02	0.53	0.14	3.64	Readily coagulated into large curds.
Woman ...	1.03	1.26	1.13	3.78	Not readily coagulated; forms small curds.
Ass.....	0.67	1.55	2.31	1.64	

It is a striking fact that in the above table the milks are arranged in order of their digestibility by infants, which corresponds with their relative degree of colloidal protection. Thus, A. Jacobi ["The Intestinal Diseases of Infancy and Early Childhood," N. Y., 1889] stated that asses' milk has been recognized

\* It is probable that of some the milk fat is in colloidal dispersion.

as a refuge in digestive disorders in which neither mothers' milk nor cows' milk nor mixtures were tolerated.

The addition of protective colloids to cows' milk stabilizes it and makes it behave like mothers' milk, when treated with acid or rennin. In modifying cows' milk for infant feeding, the usual dilution, followed by an adjustment of the fat and lactose ratios, is, of course, necessary. If enough protective colloid be added, coagulation of casein in the stomach may be entirely prevented, or, at least, the coagula kept in a very fine state of subdivision.

Besides stabilizing the casein, protective colloids have a very important effect on the milk fat, on which they exercise an emulsifying and emulsostatic influence. Indirectly their stabilization of the casein is of much greater importance, because insufficiently protected casein in curding, entraps mechanically most of the milk fat, making a fatty, greasy curd which tends to repel the acid gastric juice and pass undissolved or only partially dissolved into the intestine, where its putrefaction causes trouble.

It is probable that the relative percentage of lactalbumin decreases with the period of lactation, so that the milk of a herd is in this respect more uniform than the milk of a single cow. With nervous women, nervous shock probably decreases the amount of albumin secreted, and this would register itself in a digestive upset in the nursling. The protective ratio of any particular mother's milk is an important factor in its usefulness to the infant.

Although their action was not perfectly understood, the most diverse kinds of protective colloids have for years been used in the modification of cows' milk for infants. For over thirty years Jacobi advocated the use of gelatin and gum arabic, and the use of cereal gruels and dextrinized starch is familiar to all. Beer (especially dark dextrinous beer in Bavaria), seaweed (Irish moss) and lichens (Iceland moss) are among the protective colloids used in other lands, and in England especially, sodium citrate is much used. This protective salt, when going into solution, exhibits in the ultramicroscope actively moving ultramicros, a fact indicative of its colloidal condition.

The action of protective colloids is beautifully illustrated in the ultramicroscope, which enables us to see, in very highly diluted milk, the individual colloidal particles of casein in active motion, and to watch the course of their coagulation by acid or rennin. The casein ultramicros of cows' milk first form groups

of two or three, whose motion is somewhat hampered, and they continue to aggregate into larger and still larger groups whose motion decreases as their size increases, until they finally sink out of solution in coagulated masses. If, however, some gelatin or gum arabic solution be added to the diluted milk before the addition of the acid or rennin, the casein particles continue their active "dance" and do not coagulate. In this connection it is interesting to note that the casein particles of mothers' milk appear to be much smaller than those of cows' milk, probably because of the more highly protective medium in which they are formed and exist. [See J. Alexander, *Kolloid-Zeit.* 1909, 1910; *J. Am. Chem. Soc.* 1910, 28, 280; Alexander and Bullowa, *Arch. Pediat.* 1910; *J. Am. Med. Assoc.* 1910.]

Since E. Zunz showed that certain albumoses exerted a coagulative rather than a protective action, J. Alexander digested lactalbumin with rennin or rennet, and found that the resulting digestion products no longer acted as protectors in forming and stabilizing colloidal precipitates (for example,  $\text{AgCl}$ ), but actually tended to act as coagulator. He therefore advanced the following simple colloid-chemical explanation of the rennin coagulation of milk [8th Int. Cong. Appl. Chem 1912, 6, 12-14]: (1) The enzyme rennin digests the lactalbumin, thereby destroying its protective action; (2) the resulting albumoses are probably coagulators; (3) calcium salts liberated from their adsorption by the lactalbumin and the like also aid in the coagulation.

When cream, or milk, heated to 50 to 60 deg. C. is forced through tiny orifices under great pressures (the pressures used are 200 atmospheres and more, and the fluid is usually spattered against an agate plate), the fat globules are much more finely dispersed, being reduced to about one hundredth their former diameter. As a consequence of the enormous increase in the free or specific surface of the system, the viscosity of such *homogenized milk* is greatly increased. The finely divided fat adsorbs so much lactalbumin (Wiegner estimates that it adsorbs about 25 per cent., as against about 2 per cent. in ordinary milk), and is so highly stabilized thereby, that homogenized milk will not yield butter on churning, nor does homogenized cream churn or whip. On the other hand, because of its viscosity, homogenized cream with 17 per cent. butter fat will make as well-bodied an ice cream as an ordinary 25 per cent. cream. In fact cream is now largely kept

in cold storage in the form of sweet butter, which is homogenized with sweet milk in the busy season, yielding cream again.

In *whipped cream* coagulation of the lactalbumin may be a factor too, and with Charlotte Russe and Bavarian creams gelatin is added.

Artificial milks are made by emulsifying vegetable fats or oils with protective colloids or with skim milk. Most of them are deficient in vitamins.

### ICE CREAM

One of the essentials in ice cream is that when it is served it shall have a smooth, mellow, velvety texture, and it is a fact amply proved by the experience of practical ice cream manufacturers and housewives, and backed by the authority of even very old cook books and recipes, that ice cream made without the addition of eggs, gelatin, or some similar protective colloid, is gritty, grainy, or sandy, or else soon becomes so on standing. The original standards for ice cream, promulgated under the Food and Drugs act, took no note of these facts, and fell when they were brought out in court during an attempt to justify this standard.

The added protective colloid tends to inhibit the crystallization of the water with the formation of sharp spicules of ice. Furthermore, it also stabilizes the casein, a matter of the highest importance; for as ice cream always contains considerably more fat than milk, the curds formed by unprotected casein would be particularly greasy and hard to digest.

A very misleading impression has been given by some food officials referring to gelatin in ice cream as a "filler," which naturally leads to the idea that it is an inferior ingredient added in quantity to cheapen the product. But as gelatin is expensive and as only about 0.5 per cent. is used, such a view is erroneous. The food value of gelatin as a protector of the body's nitrogen being generally admitted, and its effect being very beneficial from a digestive point of view, its use in ice cream is necessary, legitimate and scientific.

### CONFECTIONERY

Originally "gum drops" were made with gum arabic as a protective colloid to prevent the crystallization of the sugar and give the candy a smooth agreeable body. For cheaper grades

glucose and soluble starches are now used; for, although the soluble starch is not a powerful protector, it is inexpensive, considerable can be used, and commercial glucose has but slight tendency to crystallize as about half of its dry weight consists of a highly dispersed and protective dextrin. "Glucose" containing too much dextrose crystallizes on standing.

"Marshmallows" are usually made with gelatin as the emulsifying, body-forming, protective colloid, but albumen and gum are also used.

In molding candies a super-dried starch is used containing only a few per cent. of moisture. Its powerful attraction for moisture tends to keep the candy in shape. Our ordinary fruit jellies and jams contain protective colloids such as pectin, which not only give body, but usually prevent the crystallization of the large quantity of sugar present.

Nougat types of candy were originally made by stirring into a hot portion of the batch a cooler portion into which had been incorporated egg albumen, whipped to a froth. The very hot portion coagulates the albumen and fixes the air, giving a fluffy but "chewy" candy. Recently, lecithin (derived from soya beans) has been used to emulsify fats. For example, it prevents the formation, in butter-brittle, of a surface layer of fat which would soon become rancid. It is also used in chocolate coatings. The tendency of fudges to crystallize and become "grainy" may be overcome by addition of milk; but too much milk will give a caramel- or toffee-like product.

### GELATIN AND GLUE

When bones, hide, or skins are heated with water, especially after a preliminary treatment in lime water followed by thorough washing, there is formed a solution that gelatinizes when cold. If the raw material is carefully selected and treated, it yields when dried a light colored transparent gelatin; if made without the precautions that should surround a food product, the result is glue.

Since the gelatins from different sources vary considerably in the percentages of amino-acids they yield on hydrolysis, it seems obvious that gelatin is not a definite chemical entity, but is rather an adsorption complex whose structure is at least duplex and is

probably even more complicated. The various constituents of the gelatin bear a cumulative protective relation to each other (see p. 158).

Gelatin exhibits its minimum degree of swelling at its isoelectric point, about pH 4.7, and a maximum of swelling at about pH 3, after which more acid causes contraction again. J. Loeb has explained this and many other phenomena exhibited by gelatin on the basis of the Donnan theory of membrane equilibrium, assuming that the gelatin forms salts having a non-diffusible ion (see "Proteins and the Theory of Colloidal Behavior," 1922). The facts are just as well explainable on the basis of a kinetically balanced adsorption, and in view of the variable composition of gelatin, it seems idle to speak of definite salts like "gelatin chloride" or "sodium gelatinate." The presence of small amounts of adsorbed impurities, tenaciously held, exercises a marked effect. For this reason the so-called "water absorption test" for gelatin and glue is uncertain.

Generally speaking, the binding strength of a gelatin or glue is measured by its relative jelly strength and the viscosity shown by its solution; but the variations in these two factors do not always parallel each other. Heating causes a breakdown of the gelatin into smaller complexes; this lowers viscosity, jelly strength, and binding power, indicative of a drop from the zone of optimum colloidalilty. On the other hand, as glue solutions cool and the colloid begins to form large aggregates, the adhesiveness also falls off (see p. 146). In choosing a glue or a gelatin for any specific purpose, *all* of its qualities and attributes must be taken into consideration, for foam, grease, color, odor, etc., may be of crucial importance (for further details see Am. Chem. Soc. Monograph "Glue and Gelatin," by J. Alexander; also "The Chemistry and Technology of Gelatin and Glue," by Dr. Robert H. Bogue.)



## CHAPTER XV

### PRACTICAL APPLICATIONS (*Continued*)

#### GLASSES

WHILE glasses consist of mixtures of silicates containing dissolved or finely dispersed impurities or additions, and while individual silicates may be isolated from glass, the constitution of the glass as a whole is not quite so simple as might be assumed from paper formulas. For it is the physical properties of glass that are the most important, and while these naturally change as the ingredients vary in kind and proportion, still the properties of parts of one and the same batch may differ widely if they are subjected to different heat treatment. Thus *Prince Rupert drops*, made by dropping part of the clear fluid batch of opal glass into water so that the surface was quickly chilled from 1200 deg. C. down to 20 deg. C., were clear at the exterior, becoming progressively more opalescent toward the center. Slowly cooled drops of the same batch were quite opaque throughout. (See also p. 258.)

The composition of glass is so chosen that the several silicates mutually interfere with each other's crystallization (*cumulative protection*), the result being a colloidal mass in which the tendency toward crystallization may register itself by *devitrification*, a formation of relatively large crystals which render the glass turbid and injure its usual working properties.\* While many silicates may be cooled quite slowly without crystallizing, the silicates of calcium, magnesium, and aluminum form crystals if not quickly chilled, which is rather difficult to do because silicates in general have high thermal capacity but low thermal conductivity.

Tammann (Zeit. Elektrochem. 1904, 10, 502) has pointed out three main factors controlling the behavior of supercooled

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\* According to B. E. Warren (Ind. Eng. Chem. 1935, 27, 966-71) Pyrex glass after annealing for 2 years at 430° showed on X-ray examination only slight increase in regularity of atomic distribution, but no crystallization.

melts: (1) The specific crystallization capacity (measured by the number of crystallization centers formed in per unit mass per unit time); (2) the speed of crystallization; (3) the variation in viscosity. To these must be added a fourth; mutual or cumulative protection.

Every substance in forming macroscopic crystals must of necessity pass through the colloidal zone, in which surface forces (adsorption, surface tension) exercise a controlling, if transient, influence that may be made permanent if sudden cooling increases the viscosity sufficiently. The adsorption of the various silicates by each other as they reach colloidal dimensions introduces a time-lag which becomes cumulative as the several silicates protect each other, and greater as the viscosity increases. Batches of glass are so proportioned as to make this time-lag ample to prevent crystallization at the temperatures and during the times of melting, casting, molding and so on. When glass is cooled from the plastic to the rigid state, as in blowing, drawing, casting, etc., and especially when optical glass is being slowly cooled in melting pots, devitrification may occur through the separation of spherulites or minute crystals finely dispersed throughout the glass. The spherulitic form is usually indicative of crystallization in the presence of a protector, and the fact that the crystals are by microscopic examination usually found to be tridymite and cristobalite, points to the probability that some of the silica dissolves colloiddally in the molten silicates. Sulphates, chlorides, an excess of arsenic, and sometimes fluorine, facilitate devitrification, thus exercising a "salting-out" action.

Many transparent colored glasses owe their color to the presence of colloiddally dispersed substances, usually metals or their oxides. The gold ruby glasses were carefully investigated by Zsigmondy ["Colloids and the Ultramicroscope," Ch. XVII (trans. by J. Alexander), J. Wiley & Sons Co., 1909]. When gold is added to a batch of glass (usually 0.03 to 0.01 per cent. of gold chloride), the melt is colorless and may even remain so on slow cooling unless the batch is regulated to prevent this. All batches, however, if quickly chilled, are colorless and optically clear in the ultramicroscope. The color is developed by reheating the colorless glass to the softening point, whereby the dissolved or crystalloiddally dispersed gold begins to separate out upon nuclei ("crystallogens") already formed in the colorless glass.

If the composition and heat treatment of the batch has been such as to yield a large number of small nuclei, the color developed is a bright ruby red; for although each of these amicroscopic particles grows to colloidal dimensions, the available gold is used up before any of them become big enough to render the glass turbid. On the other hand, if a small number of larger nuclei be present in the colorless ruby glass, development leads to a dirty blue or turbid maroon shade because the dissolved gold is deposited in fewer and larger masses.

The subjoined Fig. 16 shows the results of Zsigmondy's ultra-microscopic examination of good and of spoiled ruby glass. Both specimens had been cooled slowly and reheated more rapidly until one began to melt (hot end) while the other end remained cold (cold end). The fact that the average distance between ultramicros remained constant in all parts of the specimens proves that the reheating formed no new nuclei.

Hot End		Good Ruby Glass		Spoiled Ruby Glass
<div style="border: 1px solid black; padding: 5px; display: inline-block;"><div style="text-align: center;">a b b'</div></div>	Color Red	Color intense red. Numerous green ultramicros, very close together, their brightness diminishing. ↓	Color D	Color blue. Ultramicros fewer, copper-red, further apart.
				Color violet. Ultramicros yellow.
	creasing ↓	Homogeneous green light cone.	↓	Color bright red. Ultramicros green.
		Colorless and homogeneous.		Colorless. Few faint specks visible.
Cold End				

Fig. 16.

H. F. Bellamy's results (J. Am. Ceramic Soc., 1920) show that the stannic oxide used in gold ruby glass acts as a protector to the gold, keeping the color true and deepening it so that less gold can be used. This recalls the work of Zsigmondy, who, by mixing the hydrosols of gold and stannic acid, synthesized the purple of Cassius (an ammonia-soluble deep red precipitate obtained by mixing solutions of auric chloride and stannous chlor-

ide), which Berzelius had regarded as a chemical combination of the tin sesquioxide with purplish oxide of gold.

Most "red" glasses (danger signal lights) are made of selenium glass, which is pale yellow when molten and acquires the ruby tint only on proper heat treatment. If the selenium particles aggregate too much, the glass becomes an opaque maroon, and finally a muddy orange.

Minute or colloidal crystals of doubly refracting substances when uniformly oriented in a transparent matrix, give the same polarizing effect as would a crystal of Iceland spar. Dr. Edwin H. Land informs me that "Polaroid" is a set suspension of colloidal needles of a periodide of quinine sulphate uniformly oriented in a matrix of cellulose acetate. Besides many scientific uses, the material can be used to polarize the light coming from automobile headlights, so that the driver of an approaching car, by setting a disc of the same material in opposing phase, can practically extinguish all glare.

### METALS AND ALLOYS \*

Coarsely crystalline metals are brittle, because they tend to split along the lines of crystal cleavage,<sup>†</sup> and therefore the *metallurgist usually aims to produce a fine-grained structure*. Among the physical methods used to achieve this end are chilling and rolling, while the chemical methods involve the removal of undesirable constituents (as in the conversion of pig iron into steel), and the addition of desirable constituents (carbon in case hardening, various metals in alloy steels). Thus Pütz found that the predominant effect of vanadium in steel is to decrease the size of the ferrite grains, and make the pearlitic structure fine-grained and homogeneous, yielding a harder steel. Chromium nitride also exercises a grain-refining action.

One chief cause of fine-grained structure seems to be the inhibition of crystallization by substances colloiddally dispersed in the metal. These may be other metals, such as vanadium, molybdenum, chromium, nickel or tungsten (or their compounds) in alloy steels, compounds such as  $\text{Fe}_3\text{C}$  in ordinary steel, or even the metal itself in the case of pure metals. The last mentioned

\* The author thanks C. E. MacQuigg, E.M., for helpful suggestions.

<sup>†</sup> Planes of cleavage are not necessarily the same as planes of slip. See, e.g., M. Mathieu, *Chim. et Ind.*, 1935, 33, 21 T.

phenomenon is consequent on *iso-colloidism* (a colloidal dispersion of the metal in itself as dispersing phase), which may lead to *auto-protection*, the colloidal phase tending to interfere with the crystallization of the rest. Several organic compounds exhibit a similar phenomenon, yielding amorphous gels which gradually become visibly crystalline (see p. 157). It must be remembered that size alone is the criterion of the colloidal condition. As Scherrer has shown with the X-ray spectrometer, the ultramicros and even the amicros in colloidal gold hydrosols consist of tiny crystalline groups; colloidal silicic and stannic acids showed both crystalline and random or haphazard molecular clusters, while gelatin was entirely amorphous.

### THE TIME FACTOR

With metals the crystallization forces are so powerful and act so rapidly, that a coarsely crystalline structure usually results on ordinary slow cooling. To preserve the fine colloidal structure, even in the presence of protectors, drastic chilling or quenching is often necessary.

A fact of general importance in nature, having especial application to the phenomena met with in metals and alloys, is that many transformations occur so rapidly as to elude our observation, and compel us to draw upon our imagination to follow what happens between the initial point and the end-point.\* By photographs taken thousandths of a second apart, Lord Rayleigh showed the curious differences in patterns that occur when various liquids are dropped into water.

### IRON AND STEEL †

When treated with dilute acid, drastically quenched tool steel does not separate out carbide of iron, but yields instead a complicated mixture of hydrocarbons. This shows that the  $\text{Fe}_3\text{C}$  is

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\* T. W. Richards [*Am. Chem. J.*, 26, 61 (1901)] followed microscopically by instantaneous photography, the separation of crystals from solutions, and reported that the initial growth is much more rapid than subsequent growth. V. Henri first applied the "moving picture" camera (cinematograph) to the ultramicroscope, and since then many others have made remarkable films of ultramicroscopic happenings.

† The reader is referred to "The Metallography and Heat Treatment of Iron and Steel" by Prof. Albert Sauveur (Harvard University; 4th ed. University Press, 1935). This contains many splendid photo-micrographs by Dr. F. F. Lucas and others. See especially Chapter XVIII.

in such a fine state of subdivision that upon its decomposition the nascent hydrogen and carbon are within the range of molecular attraction which is of the order of 50 millimicrons; and the  $\text{Fe}_3\text{C}$  is in colloidal state.

Such drastically quenched steel owes its great hardness to its enormous free or specific surface, but it is too brittle to be of practical use, and must therefore have its hardness drawn or reduced. This *tempering process*, as it is called, consists in reheating the steel and keeping it at certain temperatures for various times. As soon as the temperature of the steel permits, the aggregation of the  $\text{Fe}_3\text{C}$  (or cementite, as it is known), which was suspended by the previous chilling, begins anew. Metallurgists recognize the following forms of the iron-iron carbide dispersion (Table XX):

TABLE XX

Iron-Cementite Dispersions	Nature of Dispersion	Microscopic Appearance
Austenite .....	↓ "Solid solution" .....	Structureless streaks.
Hardenite* .....	Colloidal .....	Structureless martensite.
Martensite .....	Colloidal .....	Generally acicular, but varies; may be very fine.
Troostite .....	Coagulation begun .....	Rounded or wooly (globulitic).
Sorbite .....	Coagulum .....	Fine pearlite, not readily microscopically resolvable.
Pearlite .....	Coagulum .....	Laminated; may segregate into balls.

The X-ray investigations of A. Westgren and of G. Hägg (J. Iron and Steel Inst., 1934, 130, 439) have shown that in austenite the carbon atoms are dispersed in the lattice spaces between the iron atoms, giving what has been termed an "interstitial solid solution," which enlarges the "unit cell" and produces lattice-strain. But the electronic forces operative between the C and the Fe atoms are identical with chemical forces, so that we practically have ionized cementite ( $\text{Fe}_3\text{C}$ ) dissolved in  $\gamma$  iron (the allotrope of iron stable at lower temperatures).

\* This term has fallen into disuse, together with Osmandite and Lebourdite.

Hardenite is named from its intense hardness; pearlite from its pearly luster; the rest are named after the metallurgists Roberts-Austen, Martens, Troost and Sorby, respectively.

On cooling, this "solid solution" tends to undergo two changes:

(1) The hot, *face-centered* gamma allotope of iron tries to re-arrange its atoms to become the *body-centered* alpha allotope. This requires only a slip into a new lattice, without much movement of atoms.

(2) The dispersed or ionized carbon atoms try to form  $\text{Fe}_3\text{C}$  molecules. This demands more extensive atomic migration than (1); and the further aggregation of  $\text{Fe}_3\text{C}$  "molecules" into microscopically visible particles, demands still more atomic or molecular migration.

As the temperature drops, the increase in viscosity of the mass interposes an increasingly powerful barrier to the realization of these two tendencies, and the intensities of the tendencies themselves also vary at different rates.\* The structures which emerge from this conflict will therefore vary greatly with speed of chilling and with precise composition of the mass. Re-heating or tempering also exerts its effect, so that a large number of microscopically visible structures may be formed directly, or even indirectly by the heat of the polishing or of the etching reagents needed to prepare the specimen for metallographic examination. The following excerpts from "Metal Progress," Aug., 1935, indicate that *degree of dispersion is a dominant factor in the structures recognized by metallurgists*: "Of course, a sizable section of hardened steel cannot consist entirely of martensite and may also contain some retained austenite or alpha iron and cementite in some form of aggregation." (K. R. Van Horn). "From the physical point of view, pearlite, sorbite, and troostite are all the same phase—consisting of a mixture of ferrite and cementite—the difference being the degree of fineness of the cementite particles and/or lamellae." (K. Honda.) "Whether or not different stages of coalescence are better distinguished by different names is largely a matter of individual taste. Those who are inclined to such names may point to such a series as dust, sand, gravel, stones, boulders, and there is no fitting rejoinder." (J. R. Vilella, G. E. Guellich, and E. C. Bain.)

The *spheroidization* of cementite which occurs in pearlite after appropriate heat treatment, strongly suggests the guttulate

\* See p. 270 for discussion of the "stepped transformation" in steel.

or dropwise separations which so often occur in systems with fluid dispersing agents. (See p. 97.)

It is interesting to note that hardenite and martensite represent the hardest dispersions, the still finer austenite and also the coarser troostite, sorbite, and pearlite all being softer. Although the allotropic change complicates the situation, this seems to be an instance of the zone of maximum colloidality (see p. 36). Jeffries and Archer (Chem. Met. Eng., 1921, 24, 1057) used the expression "critical dispersion" in speaking of the similar phenomenon observed in the alloy *duralumin* by Merica, Waltenberg and Scott (Bull. 150, U. S. Bureau of Standards, 1919). On simple ageing at room temperature, this alloy reaches a maximum hardness and then becomes softer again. Merica, and Jeffries and Archer ascribe this peculiar hardening of duralumin to the precipitation\* of colloidal  $\text{CuAl}_2$ , whereas the British National Physical Laboratory believe that  $\text{Mg}_2\text{Si}$  is responsible. Probably both compounds are involved, and we may have here another instance of *cumulative protection*, where a protector is itself protected.

Jeffries and Archer† believe that this phenomenon in steel, an analogue of which occurs in the alloy duralumin, is due to the fact that the hard particles of the dispersed phase act as *keys*, preventing any motion along the cleavage or slip planes as a whole. While this mechanical comparison may appeal to engineers, the action of surface forces, together with the fineness of crystal grain which minimizes the length of the slip planes, is quite sufficient to account for the phenomena observed.

The enormous power of these surface forces is shown by the results of some experiments privately communicated to me by P. Scherrer of Zurich. He coagulated unprotected gold sols with electrolytes, and by X-ray examination found that the tiny ultramicros (which were about 2  $m\mu$  in diameter and showed a crystalline gold space lattice) practically fused together into homogeneous crystals of larger size. Even soft substances, if finely dispersed, will produce great increase in hardness. Thus a few per cent. of oil added to whiting makes a firm putty when

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\* Hence arose the expression "*precipitation hardening*," much used by metallurgists. However, the word precipitation involves the idea of a separation, whereas the effects of dispersion extend downward into the range of "solid solutions," and the expressions "critical dispersion" or "zone of maximum colloidality" seem preferable.

† Chem. Met. Eng., 1922, 24 1065.



ground in with it. And S. U. Pickering\* made an extremely stiff mass by emulsifying 99 per cent. of petroleum oil in 1 per cent. of soap water.

The size, shape, initial heating and chilling of the piece of steel, as well as the speed, temperature and time of its reheating or tempering and speed of its second chilling, are all factors controlling the nature of the final dispersion, which is also largely influenced by the chemical composition of steel itself (percentage of the  $\text{Fe}_3\text{C}$ , presence of other metals and of impurities).

As a consequence, the proper tempering of steel requires much experience in the practical control of conditions, otherwise the optimum point is either passed or not reached; and for most uses the optimum dispersion of the cementite lies within or just beyond the colloidal zone. The addition of manganese (m. p. 1225 deg. C.) to steel retards the aggregation of the cementite to such a degree that ordinary slow cooling yields martensite. Steels containing tungsten and other metals of high melting point are known as "high speed" steels because lathe tools made with this highly protected steel *maintain* their hardness even though brought to a low redness by the high speed of the lathe. Under such circumstances ordinary tool steel at once loses its temper.

The behavior of the iron-carbon alloys is greatly influenced by the allotropic changes of iron.

After "freezing" at about 1505 deg. C., *pure iron* shows upon further cooling a large evolution of heat at about 900 deg. C. known as *thermal arrest point* ( $\text{Ar}_3$ ), and a smaller evolution of heat at about 780 deg. ( $\text{Ar}_2$ ). Above 900 deg. the iron exists in the non-magnetic or gamma form,<sup>†</sup> and below 780 deg. in the magnetic or alpha form, which exhibits a different crystallization from gamma iron. Between these temperatures, Rosenhain believed that the iron exists in a third allotropic form, known as beta iron, which has the crystal form of alpha iron but is non-magnetic like gamma iron. Benedicks, on the other hand, believes that the evolution of heat at 780 deg. does not indicate the change of a beta allotrope into gamma iron, but represents the final disappearance of persistent gamma iron molecular groups from the metal.

\* *J. Chem. Soc.*, 1902, 91, 2002.

† A new form, delta iron, is claimed by Honda to exist at higher temperatures.

These apparently conflicting views can be reconciled by regarding the iron between 900 deg. and 780 deg. C. as an *allocalloid* or *allodispersoid*, the so-called "beta" iron being an alpha-gamma adsorption compound (alpha iron dispersed in gamma iron), whose breaking up into the more completely orientated alpha iron sets free the relatively smaller amount of heat at the point  $Ar_2$ . This view accounts for the following facts: (1) Beta iron has the same crystal form as its "predominant partner," alpha iron, but is not magnetic;\* (2) gamma iron dissolves carbide, whereas beta iron and alpha iron do not; whatever gamma iron exists in the beta zone is adsorbed by or in some loose kind of combination with the dominant alpha iron, and is not free to exert its solvent action on iron carbide; (3) the increase in strength when alpha iron is transformed into beta iron; as the temperature goes over 780 deg. C., some gamma iron forms, and the resulting alpha-gamma adsorption compound increases the total free surface and strength of the system; (4) the fine acicular structure of beta iron; this is indicative of crystallization in the presence of a colloid.

### STEEL

The preceding remarks apply to pure iron. With the introduction of carbon, we have to deal with the iron carbide  $Fe_3C$  (cementite), and the system is complicated accordingly, dislocating the thermal arrest points.

A *low-carbon steel* (containing, say, 0.2 per cent. of carbon which dissolves in the liquid iron when cooling down to 840 deg. C. consists of an apparently homogeneous solid solution or dispersion of cementite ( $Fe_3C$ ) in gamma iron. At 840 deg. C. the alpha-gamma dispersion forms ( $Ar_3$ ), and at 750 deg. C. the residual alpha-gamma adsorption compound decomposes into alpha iron ( $Ar_2$ ). The steel now consists of alpha iron crystals dispersed in a "solid solution" of iron carbide in gamma iron. With further cooling the quantity of alpha iron crystals increases until at a little below 700 deg. C. the remaining gamma iron-cementite solid solution is transformed into a eutectoid mixture of

\* Magnetism seems to depend not on chemical composition, but rather on a peculiar regular molecular orientation. The so-called "Haeussler alloys" are magnetic, although their individual constituents are not. According to A. W. Hull [Phys. Rev., 14, 540 (1919)], magnetism depends on the distance between atoms rather than their arrangement. Recently, the concept of " $\beta$  iron" has been abandoned—see e.g., Colin J. Smithelle, "Impurities in Metals" (1928).

alpha iron (ferrite) and iron carbide (cementite) with an evolution of heat ( $Ar_1$ ).

This last transformation seems to be the breaking up of an adsorption compound between gamma iron and iron carbide, the former transforming into alpha iron and the latter being set free to form aggregations of its own. This adsorption compound carries over some of the gamma iron through the so-called "beta" zone to the eutectoid point, where, with increasing carbon content, increasing quantities of heat are evolved. The allotropic transformation of the iron becomes practically negligible when the steel contains above about 0.5 per cent. of carbon (which, however, means about 7.5 per cent.  $Fe_3C$ ). Steel of eutectoid composition (about 0.9 per cent. C, equaling about 13.5 per cent.  $Fe_3C$ ) exhibits only a single thermal arrest point, at which it glows visibly. This phenomenon, known as *recalcescence*, indicates a sudden large release of energy consequent to the breakdown of the extensive metastable system gamma iron-cementite, whereby two delayed transformations occur simultaneously—the iron transforms from gamma into alpha iron (ferrite), and at the same time the released cementite aggregates. The inhibition of the allotropic iron transformation shows that in *eutectoid steel* the large percentage of  $Fe_3C$  has carried over practically all the gamma iron in metastable condition to the eutectoid point. The presence of such elements as silicon and manganese perceptibly changes the location of the eutectoid point, illustrative of the easy disturbance of colloidal systems by foreign substances.

The iron carbide (cementite) possesses considerable cohesion and attempts to aggregate against the resistance offered by the now highly viscous iron—an ideal condition for the development of a colloidal system. The cohesive power of the cementite is so great, however, that in unquenched steels it usually appears interspersed with alpha iron (ferrite), as fine plates or fibrils, yielding the finely laminated structure known as *pearlite* because under proper illumination it exhibits the iridescence of mother of pearl. The iridescence like that of a diffraction grating, is evidence of the fineness of the pearlitic structure, which, like the diatom *Pleurosigma*, taxes the highest powers of the microscope for its resolution, the lamellæ being often less than 0.2 micron apart.

Fig. 17 illustrates the relation between time required for onset and completion of transformation at constant temperature

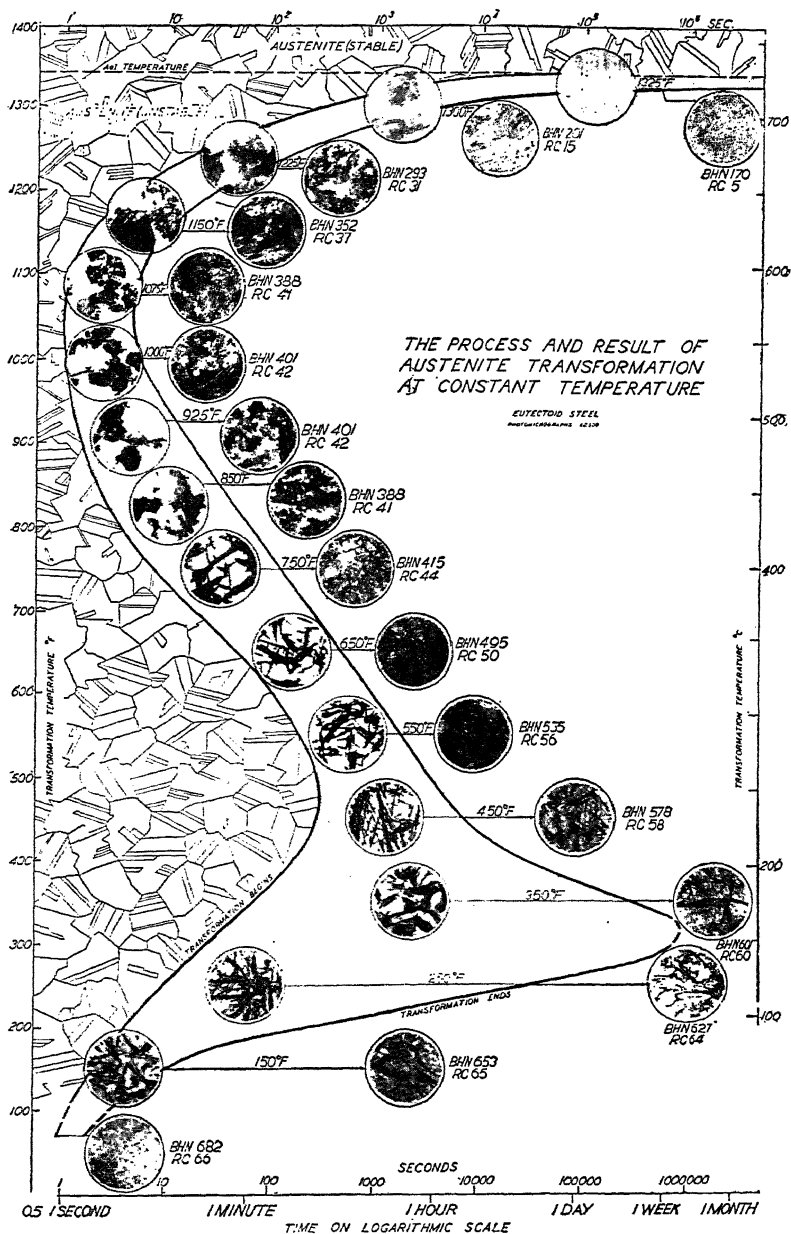


Fig. 17. (Courtesy of Research Laboratory, U. S. Steel Corporation.)

(plotted as abscissae) and the temperature (plotted as ordinates) in the case of a eutectoid steel. (0.85% C.)

Micrographs in the shaded band represent the structure when the transformation has gone half way; those to the right represent the final structure at the corresponding temperature. These demonstrate that the precise structure depends upon the temperature of transformation. The hardness of the final products is given in both Brinell and Rockwell "C" units (R). Note that the finest dispersions are the hardest.

Microscopically, eutectoid steel (about 0.9 per cent. C.) when slowly cooled, consists entirely of pearlite, thus corresponding to the pure eutectic of ordinary alloys.\* But with very slowly cooled

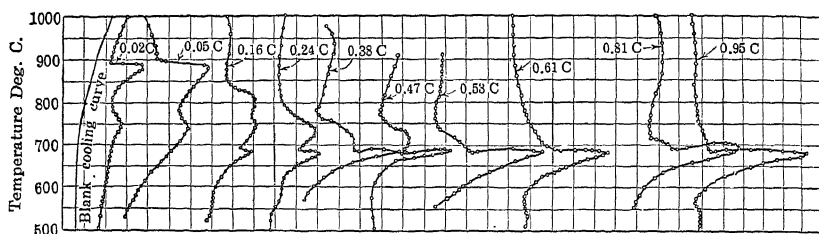


Fig. 18. Changes in thermal arrest points of steels with increasing carbon content.

steel, or with steel reheated for a long time at about 700° C., the cementite tends to form balls or globules (spheroidization), the liberated ferrite at the same time forming larger crystals.

Table XXI, page 269, shows the inter-relation of these phenomena.

The cooling curves (Fig. 18) taken from Prof. H. C. H. Carpenter [Engineering, 1919, 107, 341] show how with growing carbon content the three thermal arrest points are combined into one in eutectoid steel.

### STEPPED TRANSFORMATION IN STEELS

The aggregation of cementite takes time and there is always a time lag in the process. Consequently when carbon steel is rapidly cooled, the  $A_1$  transformation takes place at a lower temperature than when it is slowly cooled. This drop increases with

\* As the Greek-derived word indicates, a eutectic is *the most easily fusible mixture* of two metals or other substances.

TABLE XXI  
CONDITION OF STEEL AT VARIOUS TEMPERATURES

Pure Iron	0.2 Per Cent. Steel	0.9 Per Cent. Steel
Gamma iron.....	Gamma iron-cementite solid solution.	This is eutectoid steel. So much cementite is present that no alpha-gamma adsorption is formed, the gamma iron being held in metastable condition by the cementite, down to Ar <sub>1</sub> .
700 deg. C. Gamma iron forms alpha-gamma adsorption compound. Largest thermal point.	840 deg. C. Alpha-gamma compound forms (Ar <sub>2</sub> ) late because of cementite.	
Allocoloidal Zone.	750 deg. C. Alpha-gamma compound changes to alpha iron.	
780 deg. C. Alpha-gamma compound decomposes into alpha iron.	700 deg. C. Gamma iron-cementite "adsorption" compound decomposes, gamma iron changes to alpha iron, and cementite is liberated and aggregates.	700 deg. C. Sudden change of all the iron from gamma to alpha, with liberation of all the cementite.
Alpha iron.	Alpha iron and cementite.	Pearlite.

the speed of chilling until it reaches about  $600^{\circ}\text{C.}$ , when still more drastic chilling lowers it *discontinuously* to about  $300^{\circ}\text{C.}$  or less.

This *stepped  $A_1$  transformation* as it is known, is beautifully explained by Kôtarô Honda who showed that it is due to the fact that in the inhibited zone the viscosity of the dispersion medium is sufficient to stop the aggregation of the cementite, but that below this zone the aggregation forces of the cementite become so powerful that they then overcome the resistance of the iron, notwithstanding the fact that its viscosity has likewise increased by

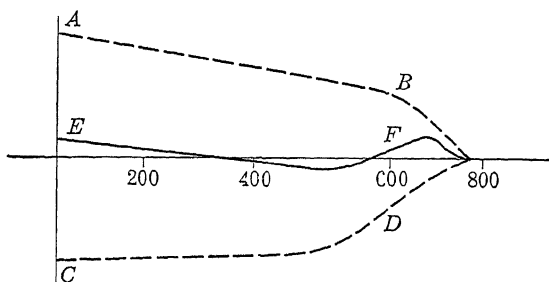


Fig. 19. Aggregation-viscosity curves, with resultant showing aggregation inhibited between about  $600\text{--}300^{\circ}$ . AB = aggregation tendency curve; CD = resistance curve; EF = observed resultant.

cooling. The following curve (Fig. 19), taken from Honda's paper shows how two factors operating at various rates over a temperature range, may cause puzzling results, unless their effects can be separately analyzed.

AB is the transforming tendency or aggregating curve, plotted positively; EF is the resultant, which represents the extent to which the tendency is able to establish itself against the resistance, CD.

### TIN-LEAD ALLOYS

All mixtures of tin (m. p.  $232^{\circ}\text{C.}$ ) and lead (m. p.  $327^{\circ}\text{C.}$ ) melt below  $327^{\circ}\text{C.}$ ; the alloy, 63 per cent. tin and 37 per cent. lead, has the lowest melting point. If the metals are mixed in other than these *eutectic* proportions, the excess metal tends to crystallize out alone, leaving the largest possible amount of eutectic, which solidifies later. Microscopic examination shows

that the eutectic is not a chemical compound; it is usually laminated and can be brought into relatively coarse dispersion by slow cooling.

But some forces do control the formation of the eutectic. As the fused alloy approaches solidification, lead, having the higher melting point, begins to form molecular groups or tiny crystals ("crystallogens"). This aggregation of lead molecules is opposed by the more fluid tin, thus lowering the freezing point of the mixture. Diminishing thermal agitation finally allows the tin to begin to form groups, and a stage is reached where both metals exist largely in colloidal state.\* In this zone a colloidal adsorption compound is formed, the ratio, 63 tin to 37 lead, being consequent on their specific electronic fields; any excess of tin or lead is free to crystallize independently. In the eutectic, the lead, by adsorption, interferes with the crystallization of the tin to such an extent that, if quickly cooled, the eutectic structure is extremely fine.

As with all colloids, this represents a metastable condition, and if the temperature is kept within limits which permit molecular orientation without disruptive thermal agitation, the eutectic undergoes a gradual syneresis analogous to coagulation or demulsification; a further separation into its constituent phases. The laminated structure, common in eutectics, already represents the aggregation of the preëxisting colloidal dispersion, as has been especially pointed out in the discussion of pearlite in steel.

*Solder*, used by plumbers and others, is an alloy consisting of about equal parts of tin and lead. At about 210 deg. C. it begins to extrude crystals of lead into the still fluid eutectic cement, rendering it pasty like putty, and easy to "wipe," spread or mold into the desired shape. The introduction of the highly crystalline antimony (m. p. 630 deg. C.) into tin-lead alloys results in the early formation of crystals of antimony or of the hard brittle compound Sn-Sb, with the result that the ternary alloy is much harder.

*Type metal* is one of these ternary alloys whose composition varies with price and service conditions. It is usually chilled quickly, which is conducive to fine structure and hardness. White

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\* All pure metals in solidifying pass through an isocolloidal zone, the narrowness of which is indicated by the sharp peak or cusp in the inverse-rate curve. See W. Rosenhain, "Introduction to Physical Metallurgy, pp. 85-87. D. Van Nostrand Co., N. Y., 1914.



bearing metals, on the other hand, are usually cast in larger masses and chill more slowly; their composition is chosen to yield hard wear-resisting crystals of Sn-Sb embedded in a colloidal plastic eutectic, which can adapt itself to the bearing's irregularities of shape and pressure.

### ZINC-COPPER ALLOYS (BRASS)

*Brasses* containing less than 30 per cent. of zinc, irrespective of their speed of chilling, always consist of a "solid solution" of zinc in copper, known as alpha brass.

This alpha brass is really an adsorption compound between copper and zinc, in which the large percentage of difficultly fusible copper (m. p. 1083 deg. C.) aggregates so rapidly that even in so-called "quickly cooled" specimens, the zinc (m. p. 419 deg. C.) is for the most part too finely dispersed to be much adsorbed by the copper. Hence the alloy exhibits a dendritic structure showing a copper crystallization as modified by adsorbed zinc, the amount of which increases from the center outward as the copper aggregates and the mother liquor becomes richer in zinc.\*

As Rosenhain observes, the percentage of each metal and its state of aggregation are momentarily varying during cooling, and because of the wide disparity between the melting points of the two metals, homogeneity is favored either by extremely rapid quenching from fusion (which tends to prevent the copper from aggregating) or by slow cooling and annealing, which favor the more complete dispersion and adsorption of the zinc (which is segregated by ordinary cooling).

The natural desire to introduce more of the cheaper zinc into brass is limited by the fact that with brasses containing 30 to 37 per cent. of zinc there appears a new, hard, brittle metastable phase, beta brass. Such brasses if quickly cooled are relatively hard and brittle, but if cooled slowly the beta phase disappears. With more than 37 per cent. of zinc, the beta phase is stable at all temperatures down to 470 deg. C. and the slowly cooled alloys exhibit the duplex structure found in *Muntz metal* (approximately 40 per cent. zinc). Carpenter believes that below 470 deg. C. the beta phase decomposes into alpha and gamma

\* Small pieces of alpha brass drastically quenched from fusion in liquid air will probably appear homogeneous in the microscope.

phases, and in fact that the beta phase is an almost ultramicroscopic mixture of alpha and gamma brass. (This indicates colloidal dispersion, favorable to hardness.)

Rosenhain [*lib. cit.*, p. 145] says that the gamma brass "is exceedingly hard and brittle and its presence in the alloys renders them useless for any purpose where strength and toughness are required. This is a typical example of a law very widely applicable to alloys, *viz.*, that those phases of a binary system which contain the two elements in anything like equal proportions are hard and brittle, only the alloys near the ends of a series being as a rule sufficiently strong and ductile to be of practical utility. We have already seen that the beta phase is harder and more brittle than the alpha, so much so that the best brasses, in which strength and ductility are of importance, are generally made with a zinc content of approximately 30 per cent., this being the cheapest alloy which does not contain the beta phase."

With solutions, as von Weimarn has shown [*Kolloid-Zeit.*, 1908, 3, 282; *ibid.*, 1909, 4, 27], medium concentrations are favorable to the development of large crystals, whereas dilute and concentrated solutions both tend to yield colloidal dispersions; and a similar condition appears to exist with mixtures of pure metals. At both ends of the alloy series appear the larger amounts of the so-called "amorphous" phase of the metal, which in most cases is stronger at ordinary temperatures than the crystalline phase. Highly crystalline metal, deficient in the colloidal "amorphous" phase, is weak because it tends to split along the planes of crystal cleavage. We should therefore expect weakness where the component metals of a binary alloy are about in equal proportions, for this concentration works against the development of colloidal metal and in favor of the larger, more perfect, but weaker crystals.

## BRONZE

In their article on "Alloys"\* Roberts-Austen and Neville, in speaking of the copper-tin alloys containing less than 9 per cent. by weight of tin, say that upon quickly chilling small ingots from successively lower temperatures beginning just above the melting point, we thus learn that these alloys (bronzes) "although chemically uniform when solid, are not so when they begin to

\* Encyclopedia, Britannica, 11th ed., Vol. 1, p. 706.

solidify, but that the liquid deposits crystals richer in copper than itself, and therefore that the residual liquid becomes richer in tin. Consequently, as the final solid is uniform, the crystals formed at first must change in composition at a later stage. We learn also that solid solutions which exist at high temperatures often break up into two materials as they cool. . . ." The work of Beilby on plastic flow and of Benedicks on quick chilling, give an insight into the behavior of metals when stressed, worked and hardened.

#### SOME RESULTS OF X-RAY EXAMINATION OF METALS AND ALLOYS

The rich fund of information given by *metallography*, the microscopic study of metals and their alloys, has been enormously extended by the facts revealed by modern X-ray investigation. The photographic pattern formed by passing a monochromatic X-ray beam through any specimen is absolutely characteristic of that particular material, and shows (1) if it is crystalline or amorphous; (2) the crystallographic system and the precise location in the *unit cell* of the constituent atoms, ions, molecules, or assemblages of these; (3) if random or preferred orientation of grains exists within the aggregate; (4) if it is a single chemical individual, a mixture of individuals, or a solid solution; (5) the size of the grains or particles, the thickness of a film, and whether there exists distortion or strain. Most substances formerly believed to be "amorphous" can be shown to possess some structural orientation. A substance which is amorphous to X-rays would give a uniformly fogged plate; but even liquids produce diffraction halos indicative of transient molecular arrangement in the course of thermal agitation. (See G. L. Clark, in Alexander's "Colloid Chemistry," Vol. III, pp. 27-40.)

In his lecture before the Institute of Metals (J. Inst. Metals, 1935, 46, 275-99), Prof. W. L. Bragg (Victoria University, Manchester, Eng.) has given a summary of the basic principles which have at present been deduced from the X-ray data regarding atomic arrangement in metals and alloys. The arrangement has two features, which may to a large extent be considered independently: (1) the pattern of sites characteristic of each phase; (2) the mode of distribution of the constituent atoms amongst the phase-sites. The diagram which shows the various phases that form when two metals are alloyed in varying proportions, has

regions where the alloy is apparently homogeneous, though its properties undergo a continuous change with the continually changing percentage composition. There are also two-phase regions, where the alloy has two constituents of constant composition (representing the phases on either side of the region), but their relative proportions vary with the percentage variation of the alloy. "The regions of a single phase may be wide, persisting over an extended range of composition; they may, on the other hand, be so narrow that they simulate definite chemical compounds."

In isomorphous chemical compounds one element takes the lattice position of another. *But with phase patterns in metals*, a substituent element often takes quite a *different* position in the lattice so that the gross phase-pattern may be maintained, thus indicating a wide difference from ordinary chemical compounds, an *independence of direct bonds between neighboring atoms*.

W. Hume-Rothery (J. Inst. Metals, 1926, 35, 315) observed that if a metal, *e.g.*, copper is alloyed with other metals of different valency, the phase diagram shows a similar series of phases. The higher the valency of the alloying element, the smaller the atomic percentage needed to reach a corresponding point in the diagram. This led to the formulation of the Hume-Rothery rule that *similar phase patterns have the same ratio of free electrons to atoms*. Metal atoms generally supply free electrons as follows:

Cu, Ag, Au .....	1 electron
Mg, Zn, Cd, Hg .....	2 "
Al .....	3 "
Sn, Si .....	4 "
Fe, Co, Ni Ru, Rh, Pd Os, Ir, Pt } .....	0 "

The theoretical basis of the Hume-Rothery rule has been developed by H. Jones (Proc. Roy. Soc., 1934, (A), 144, 225-34). It confirms the view that a phase is a pattern of *atomic sites*, rather than a chemical compound in the ordinary sense. "Interstitial replacement is found in alloys of certain metals with hydrogen, boron, carbon, and nitrogen, which must be relegated to a separate class."

A limited number of characteristic atomic phase patterns appear repeatedly in alloy systems. These are:

TABLE XXII

Phase	Structure	Ratio Electrons/ Atoms	Examples
$\alpha$	Face-centered cubic		
$\beta$	Body-centered cubic	$3/2 = 1.5$	(Cu,Ag,Au)Zn; Cu <sub>3</sub> Al; Cu <sub>3</sub> Sn; Cu <sub>3</sub> Be; AgMg; (Co,Ni,Fe)Al
$\beta'$	Complex cubic, 20 atoms per unit cell	1.5	Ag <sub>3</sub> Al; Au <sub>3</sub> Al; Cu <sub>3</sub> Si; CoZn <sub>3</sub>
$\gamma$	Complex cubic, 52 atoms per unit cell	$21/13 = 1.61$	(Cu,Ag,Au) <sub>3</sub> (Zn,Cd) <sub>3</sub> ; Cu <sub>3</sub> Al; Cu <sub>3</sub> Sn <sub>3</sub> ; (Fe,Co,Ni,Pd,Pt) <sub>3</sub> Zn <sub>21</sub>
$\epsilon$	Hexagonal close-packed	$7/4 = 1.75$	(Cu,Ag,Au)(Zn,Cd) <sub>3</sub> ; Cu <sub>3</sub> Sn; Cu <sub>3</sub> Sb; Cu <sub>3</sub> Be <sub>3</sub> ; Cu <sub>3</sub> Ge; Ag <sub>3</sub> Al; Au <sub>3</sub> Al; Au <sub>3</sub> Hg; Ag <sub>3</sub> Ir

"The precise ratios  $3/2$ ,  $21/13$ ,  $7/4$ , must not be stressed . . . the characteristic phase appears when it is near the values 1.5, 1.6, 1.75."

When in a thoroughly fluid state, the atoms in an alloy are in a state of random or haphazard disorder. As the thermal agitation diminishes, they tend to assume positions of minima of potential. If slow cooling (annealing) or re-heating ("tempering") allows them to do this, they form a *superlattice* structure of selected positions in the simpler underlying phase-pattern, which leads to the appearance of new lines in the X-ray powder photograph. Again, in contradistinction to chemical compounds, all kinds of intermediate stages may exist between perfect order and complete disorder.\*

W. L. Bragg and E. J. Williams (Proc. Roy. Soc., 1934 (A), 145, 699-730) have calculated that in a metal, atoms vibrate with a frequency of about  $10^{13}$  times per second, but that their attempts

\* Ageing and cold deformation favor atomic readjustments in some cases, which may lead to embrittlement. At very low temperatures, tin suffers a "disease," which can be inoculated into sound metal, and leads to formation of a grey allotrope.

to reach their potential minima demand the local availability of a certain amount of thermal energy to overcome the energy barrier to their motion. They estimate that if a certain amount of change towards perfect order were to take place in one second at a certain temperature, *increasing* the temperature 20 per cent. would permit the same change to occur in 0.01 second, whereas by *decreasing* the temperature by 20 per cent. it would take 17 minutes; by 40 per cent., 3 years; by 50 per cent., 30,000 years.

The conclusions of Prof. Bragg have such wide implications, that they are here epitomized:

X-ray examination of the solid state imposes the need of reviewing many of the generalizations of chemistry, especially the idea of the chemical molecule and of valency bonds. The existence of "molecules of NaCl" was disproved, the crystal showing a regular alternation of  $\text{Na}^+$  and  $\text{Cl}^-$  with equal opposite electrostatic charges. "The idea of a molecule as an entity still holds in organic molecules, where direct bonds between atoms are formed, but it must be revised when inorganic compounds are considered. 'Valency' acquires a new meaning."

"The conception of molecules is still more inappropriate when applied to compounds formed by metals. In inorganic compounds, while there are no molecules, the balancing of definite electrostatic charges on positive and negative ions requires that the ratio of these ions should be represented by integers. A compound is represented by a definite formula. I must qualify this statement to a certain extent, for we know of many cases where for instance one divalent ion can be substituted to a variable extent for two monovalent ions, so that integral ratios no longer hold. In any case the balancing of electrostatic charges still imposes definite laws on the composition.

"In alloys the case is otherwise. All the constituent metals are electropositive. Though Hume-Rothery's rule and Jones' theory indicate a definite number of atoms in the unit of pattern, they make no demand that the *ratio of the atoms of different kinds should be represented by simple integers*. . . . To conclude from these singularities (superlattices) that there is a 'compound'  $\text{CuZn}$  or  $\text{AuCu}_3$ , and that excess atoms of either kind are 'dissolved' in this compound when the ratio is other than the ideal one, is misleading if interpreted too literally. Such formulae are convenient labels for phase ranges, but must not be taken to imply

that there are CuZn or AuCu<sub>3</sub> groups and separate dissolved atoms. All atoms of any one metal play the same rôle in the structure. Naturally, the theory as outlined here stresses certain aspects and neglects others. Transitional cases can be found showing how the alloy passes into a chemical compound of the usual type as other factors become more important."

### AMORPHOUS VS. COLLOIDAL THEORY

The amorphous theory of metals, advocated \* by Rosenham [lib. cit., p. 249] among others, stresses particularly the entire absence of regular orientation or crystallization in the so-called "amorphous" phase, in which the molecules are supposed to be in the random, haphazard, and mainly isolated state assumed to exist in liquids. I believe, however, that the amorphous phase consists largely, if not entirely, of molecular groups, many of which may be oriented in the form of ultramicroscopic crystals or crystal fragments; and that its properties are due, *not to the entire lack of orientation* among its particles, but mainly to the fact that *many or most of its molecular groups are of colloidal dimensions*.

In metals the molecules are very close together and have an extremely powerful cohesion and crystallization tendency, so that it does not seem possible that the "amorphous" phase can be composed entirely of isolated atoms, molecules, or even entirely of non-crystalline groups. With the most drastically chilled metal, even allowing for the high viscosity and its rapid increase, it does not appear conceivable that no tiny ultramicroscopic crystals form, or at least that there is no grouping, regular or irregular, of the metal molecules. Even with gold hydrosols, where the dispersing water exercises a restraining influence, the X-ray spectrometer shows that both ultramicroscopic and amicroscopic gold particles are crystalline.

The facts are in harmony with the conception of amorphous metal as an isocolloid—that is, as a dispersion of colloidal crystals, crystal fragments, or non-crystalline groups, forming a solid gel-like mass. The fineness of its particles and the enormous

\* Judging from the literature, since this was originally written, Rosenham abandoned the amorphous theory.

development of free surface found in all colloids are its critical factors.\*

### POLISHING AND SURFACE-FLOW—THE BEILBY AMORPHOUS LAYER

Sir George Beilby (J. Soc. Chem. Ind., 1903, 22, 1166-1177) advanced the view that when a metal is polished, there is molecular or atomic flow, whereby the crystalline structure of the surface is converted into an amorphous layer which resembles a highly viscous liquid. Recently, G. I. Finch, A. G. Quarrell and J. S. Roebuck (Proc. Roy. Soc., 1934, (A), 145, 676-81) found that a carefully polished metallic surface did not yield any regular diffraction pattern with X-rays, but gave rise to a merely random electronic scattering. On the other hand, an unsuitably polished surface yielded a diffraction pattern, and the properly polished surface, *when suitably etched*, gave a diffraction pattern characteristic of the metal. On "flashing" a fine film of zinc onto polished copper, X-rays showed the characteristic diffraction pattern of zinc, which faded and was completely gone in about 10 seconds. Successive layers of zinc vanished with increasing slowness, and the 12th deposit, after an initial weakening, remained unchanged after 4 hours. These and similar results with other metals are considered by the authors to afford a direct experimental proof of the existence of the Beilby layer and of its formation on polishing.

### ELECTRO-DEPOSITION OF METALS

The powerful effect of protective colloids on depositing metal may be readily shown by dividing a solution of lead acetate between two glasses, to one of which is added some glue solution. Upon immersing a strip of zinc in each glass, the one without the glue gives the usual bright crystalline lead "tree," whereas the

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\* For further discussion of the colloidal state in metals and alloys see J. Alexander [Proc. Am. Inst. Min. and Met. Eng., Vol. 63, 1919, and Vol. 64, 1920; Chem. Met. Eng. 1922; First Colloid Symposium Monograph, (Univ. Wisconsin) 1923]. Many of the changes that take place with sulphur are analogous to those that occur in metals. By chilling sulphur heated to 400 deg. C. in liquid air, von Weimarn [Kolloid-Zeit. 1910, 6, 250] obtained a perfectly transparent and exceedingly elastic sulphur. Here the rapid cooling results in the temporary preservation of a relatively large percentage of the viscous  $S_{\mu}$  dispersed in the more fluid,  $S_{\lambda}$ , the resulting allocolloid being a sulphur sulphogel or a solid sulphosol.



other gives a very much inhibited or amorphous looking deposit. A tin "tree" shows similar results, but if some lead acetate be added to the stannous chloride solution, the lead and tin mutually interfere with each other's crystallization. In refining metals electrolytically, new very pure baths usually give coarse-grained brittle cathodes, but this effect wears off as "impurities" accumulate or are intentionally added.

In other cases impurities even in minute percentage, are highly injurious. Thus one part of iron in five million may injuriously affect the quality of electro-deposited nickel. In the electro-deposition of zinc, antimony is especially troublesome, even in traces.

A large variety of *addition agents* are used, the essential being that the added substance must be adsorbed by the depositing metal when the latter is in the colloidal zone through which it must necessarily pass. Müller and Bahntje (Zeit. Elektrochem. 1906, 12, 317] found that copper deposited in the presence of colloids to keep it fine grained weighed 0.2 per cent. more than metal deposited without the colloid. They found that gelatin had the most powerful effect, egg albumen considerably less, and gum and starch but little action. The relative protective efficiency of these colloids parallels their protective action in the case of colloidal gold.

An observation made by J. Alexander \* is of interest here. Moissan (Comptes rend., 144, 593; J.S.C.I., 1907, 413) has noted that the addition of a little platinum to metallic mercury causes the latter to "emulsify" in water. Upon making up such an "emulsion," Alexander noticed that the supernatant fluid remained turbid upon standing, and therefore examined the fluid in the ultramicroscope, which revealed the presence of colloidal metallic particles in active motion.

### BOILER SCALE

When water is purified before injection into the boiler, any precipitate is preferably made as coarse as possible so that it can be readily settled or filtered out. But where the precipitate is formed within the boiler, exactly the opposite result is sought. Most "boiler compounds" contain such soluble colloids as dextrin,

\* J. S. C. I. 1909, 23, 280.

tannin and bark extract, and some engineers put potatoes or starch in their boilers together with soda ash. There is a story that in the early days of steam engineering when, by insistence of John Watt, very low pressures were used, an engineer put some potatoes into the boiler to have them cooked for dinner. The potatoes went into solution and were lost, but the beneficial results of their presence was noticed.

The boiler compound of the U. S. Navy (Specification of August, 1934) gives the following formula, in percentage by weight:

Anhydrous sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) . . . . .	44%
Anhydrous disodium phosphate . . . . .	47%
Corn starch . . . . .	9%

Chapter 6 of the Manual of Engineering Instructions states: "The small amount of starch used has five very important actions. First, it helps to prevent deposition of scale or sludge in the feed lines and feed heaters if the compound is fed into the feed tank. Second, it aids very materially in sweeping out the bothersome silicates and preventing their deposition as scale. Third, it is believed to have some effect on reducing the amount of corrosion. Fourth, it imparts to the sludge a fluid character which reduces largely any tendency the sludge may have to attach itself to the metal of the boiler anywhere. The sludge, therefore, will be removed more completely by the bottom blow and, when emptying and washing out a boiler, the tube ends and drums will wash quite clean and thus reduce the labor of cleaning. The starch causes any sludge deposits which remain in the boiler after it has dried thoroughly, to contract and crack up on drying. Their removal by washing and brushing is thus made easy. The fifth, last, and certainly not the least important property which starch adds to the compound, is that it definitely reduces any tendency to foaming and priming, and thereby a much drier steam is obtained. Its value in this connection alone warrants its inclusion in the compound."

These statements indicate that precipitate formed in the presence of starch and similar colloids adsorbs them and tends to remain finely dispersed and non-adherent, so that it is readily removed on "blowing down" the boiler. The formation of hard crystalline scale is thus inhibited, if not entirely prevented.

Another way of handling the inevitable separation of salts in the boiler is to add suitable negative ions, *e.g.*, carbonate, phosphate, whose calcium salts tend to form disposable sludges rather than adherent scale. The theoretical principles governing this procedure were investigated by Dr. R. E. Hall and his collaborators (See, *e.g.*, A. C. Purdy, Trans. Soc. Naval Arch. and Marine Engrs., Nov., 1933). Carbonates decompose under many operative conditions, yielding caustic soda which may cause "caustic embrittlement" of the boiler steel, and therefore phosphates are preferable. C. W. Tod (Chemistry and Industry, 1936, 55, 256) states that in practice, 5 parts of  $\text{PO}_4$  per 100,000 ensures the absence of scale. Orthophosphates (*e.g.*, di- or tri-sodium phosphate) give an immediate precipitate with calcium salts, which may block the feed lines if they are introduced into the boiler feed water, unless colloids are introduced to prevent this difficulty. On the other hand, metaphosphates and pyrophosphates must be hydrolyzed before insoluble calcium salts are thrown out with waters of low hardness. Since feed waters vary greatly in kind and amounts of impurities, each case should be given individual consideration.

### CEMENT, MORTAR, PLASTER \*

F. M. Lea and C. H. Desch in their book on "The Chemistry of Cement and Concrete" (Edward Arnold & Co., London, 1935) point out that with cements, plasters and mortars we have solid powders which, when mixed with water, show phenomena that fall into one or more of the following groups:

- (1) Crystallization from supersaturated solution, crystals interlacing;
- (2) Formation of a semi-solid mass or gel, which undergoes desiccation;
- (3) Chemical reaction, yielding crystalloids, colloids, or both.

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\* In the journal "Rock Products," May to September, 1928, will be found "A Digest of the Literature on the Nature of the Setting and Hardening Processes in Portland Cement" (Paper No. 17), by Dr. Robert H. Bogue, Director of Research, Portland Cement Association Fellowship at the National Bureau of Standards, Washington, D. C. I am indebted to Dr. Bogue for critical suggestions.

*Setting* involves the formation of a stony mass, and may be followed by *hardening* which involves diminution or loss of permeability to water.

*Portland Cement.* The main constituents of Portland cement are the following crystalline compounds: tricalcium silicate ( $3 \text{ CaO} \cdot \text{SiO}_2$ ), dicalcium silicate ( $2 \text{ CaO} \cdot \text{SiO}_2$ ), tricalcium aluminate ( $3 \text{ CaO} \cdot \text{Al}_2\text{O}_3$ ), and tetracalcium aluminoferrite ( $4 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ ). On hydration, both amorphous and crystalline hydrates are produced, and many diverse and conflicting views have been advanced, some (*e.g.*, W. Michaelis) holding that colloidal material is mainly responsible for the hardening process, while others (*e.g.*, Le Chatelier, "La Silice et les Silicates," 1914) stress the importance of the crystalline materials. The most recent investigations indicate that both colloidal and crystalloidal processes function in the development of the characteristic qualities of cement.

On hydration, the calcium silicates form amorphous masses intermixed with crystalline calcium hydroxide.\* The alumina and iron compounds yield a crystalline hydrated aluminate, and an amorphous hydrated calcium ferrite. About three-quarters of the hydrated mass consists of colloidal hydrated calcium silicates, which are largely responsible for its characteristics, though these are considerably modified by the other crystalline materials and by the colloidal calcium ferrite, which exerts a protective action. Setting behavior, however, appears to be determined primarily by crystalloidal rather than colloidal changes, but the powerful influence of colloids on crystallization must not be forgotten, especially where the relatively small amount of water makes for saturated and supersaturated solutions.

Lea and Desch (*lib. cit.*) outline the behavior of Portland cement thus: Following expansion due to hydration, there form

- (A) a metastable gel, which in part undergoes irreversible shrinkage and becomes a stable gel, the other part changing to the final crystalline product.
- (B) crystalline hydrated products,  $\text{Ca}(\text{OH})_2$ , Ca aluminate and sulpho-aluminate, which may initially have formed gels. (B) is intermixed with (A) and its alterations, in the final crystalline mass.

\* Le Chatelier describes a similar mass made by adding calcium hydroxide to dilute silicic acid sol.

Setting they attribute to the formation of the mixture of (A) and (B).

*Lime Mortar.* The setting of lime mortar is believed to be due mainly to the drying and partial crystallization of the thick milk of lime, which is only partially carbonated by the atmospheric carbon dioxide. Very old mortars (*e.g.*, Roman mortars in England) still consist of calcium hydroxide on the interior.

*Chemical Cements.* Among these is the so-called Sorel cement, made by mixing magnesium oxide and chloride, or by dissolving  $\text{MgO}$  in  $\text{HCl}$ , giving magnesium oxychloride which sets to a cryptocrystalline mass.

A mixture of sodium silicate and calcium chloride reacts to form calcium silicate and silicic acid gel, which set together and form a cement. Loose sands and gravels have been consolidated *in situ* by alternately pumping in these two solutions.

Litharge and glycerine, rubbed together into a thick paste, set to form a cement of great strength.

*Plaster of Paris.* In 1765 Lavoisier's application of the balance to chemical problems showed that in "burning" gypsum lost three-quarters of its water of crystallization, the  $\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$  becoming  $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$ , which is five times as soluble as the gypsum. The relatively small amount of water used to temper the plaster progressively dissolves the more soluble hemi-hydrate, promptly depositing it as fully hydrated gypsum, whose long interlacing crystals can be seen if a thin layer is allowed to set on a microscope slide. Van't Hoff, by measurements with the dilatometer, showed that there is an initial contraction in volume when plaster of Paris sets, followed by a smaller subsequent expansion, which tends to force the plaster into the fine details of a mould. The net expansion on setting is  $\frac{1}{2}\%$ , and is explained by Desch (*J. Inst. Metals*, 1914, 11, 102) on the basis of interior voids. An inhuman punishment, termed "*gatch*," said to have been used in ancient Persia, consisted in burying the victim in a pit with his head out, and then filling the pit with wet plaster.

Keene's cement is plaster of Paris to which has been added some salt like alum, which accelerates the set and hardens the set mass. On the other hand many protective colloids act as *retarders*, greatly delaying or even preventing the set altogether; among these are glue, gum arabic, and the product resulting from treating hair with lime. The following table shows the result of adding gelatin to plaster of Paris:

TABLE XXIII

One part water containing gela- tin—Per cent.	Time to set in minutes.	Microscopic appearance of slide.
0	40	Characteristic crystals of calcium sulphate.
1/100	50	No crystals, except in a few spots where some colloid-free solution had diffused out.
1/10	260	No crystals.*
1/4	510	No crystals.*
1/2	960	No crystals.*
1	Not set in 48 hr.	No crystals.*
2	Not set in 48 hr.	No crystals.*

\* No regular, ordinary crystals, the mass consisting of aborted, modified or sphero-crystals, or of colloidal crystals or other minute unoriented groups, or of a mixture of these. See article by J. Alexander in J. Soc. Chem. Ind. 1909, on "Colloid Chemistry and Some of its Technical Applications."

## CHAPTER XVI

### PRACTICAL APPLICATIONS (*Continued*)

#### CHEMICAL ANALYSIS \*

IN GRAVIMETRIC methods the object of the analyst is to form a non-colloidal precipitate that can be separated on a filter, washed and weighed. Von Weimarn has shown that precipitates formed in very dilute or very concentrated solutions tend to be colloidal, and for this reason the analyst usually chooses solutions of medium concentration, together with an excess of the precipitating reagent as a coagulant, acid in some cases, alkali in others. Adsorption of soluble substances by precipitates is a prolific source of error, which the analyst minimizes by thorough washing and a choice of precipitants, concentrations, and so on. The work of H. B. Weiser (Rice Institute) [*J. Phys. Chem.* 1919, et seq.] indicates what large errors may be due to neglect of precautions against adsorption.

Often when analytical methods speak of dissolving a precipitate, it is simply peptized or dispersed into a colloidal solution which passes through the filter paper. Thus the gel of aluminum hydroxide is readily peptized by alkali and that of iron hydroxide by hydrochloric acid.

Sometimes substances are added which inhibit precipitation by producing a colloidal non-filterable sol. Citrates and tartrates are especially apt to do this, and require special analytical treatment. The presence of such salts or of protective colloids (glue, dextrin, organic extractives) in technical products or specimens may lead to grave errors in analysis, so that the analyst should destroy them by oxidation or ignition, or else nullify their effects by a suitable excess of coagulant or precipitant. "Organic matter," as it is vaguely termed, may act: (1) By totally or partially preventing the formation of precipitates; for example, tartrates

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\* This topic has been treated at length by Prof. H. Bassett in 4th Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1922; also his paper in Vol. I of Alexander's "Colloid Chemistry, Theoretical and Applied," (1926).

prevent the precipitation of aluminum, chromic and ferric hydroxides [Yoshimoto, J. Soc. Chem. Ind. 1908, 27, 952]; (2) by preventing the satisfactory filtration of a precipitate when formed [Mooers and Hampton, J. Am. Chem. Soc. 1908, 30, 805] (3) by rendering precipitates difficult to wash and purify [Duclaux, J. Soc. Chem. Ind. 1906, 25, 866].

A few experiments will make this clear. Hydrochloric acid gives with lead acetate solution a heavy coagulated precipitate, but with sodium chloride, a less highly ionized precipitant, only a colloidal precipitate. If some glue solution be first added to the lead acetate, then sodium chloride produces no visible precipitate at all. In testing urine for sugar with Fehling's or Benedict's solution, as Prof. M. H. Fischer (Univ. of Cincinnati) has pointed out, the simultaneous presence of albumin (or other protective colloid) is apt to bring down the copper oxide in a yellow colloidal state which, if some of the blue copper remains unreduced, appears as a greenish turbidity. For this reason the urine is boiled and filtered before testing for sugar, to separate out any albumin.

The Wassermann and precipitin tests are best understood on the basis of colloid chemistry—adsorption, peptization, protection or lack of protection, coagulation, and so on.

## PHOTOMETRIC ANALYSIS. COLORIMETRY AND NEPHELOMETRY

These important, simple, and accurate methods of quantitative determination are based on measurement of the amount of light transmitted or diffracted by a swarm or cloud of finely dispersed solid or liquid particles, usually dispersed in a liquid. Colorimeters had long been in use, but the term nephelometry (from the Greek νεφέλη, a cloud) was proposed by Prof. T. W. Richards (Nobel laureate, Harvard University), who also devised the first nephelometer, and first used the method for estimation of minute amounts of chloride ion by formation of a cloud of AgCl. Where diffracted light is measured, the term "Tyndallometer" is also employed.

Since nephelometry is based on comparison of an "unknown" with a "standard" turbidity, both dispersions must consist of the *same substance*, in the *same degree of dispersion*, and *sufficiently stable* to permit accurate readings. Where necessary, protective



colloids may be used (See *e.g.*, H. W. Moseley, A. G. Rohwer, and M. C. Moore, "Science," 1934, 79, 507). Among the nephelometric methods of analysis are the following:

*Acetone*—precipitate produced by silver-mercury cyanide. Can be used for determination of acetone in blood, and will detect 1 part in 100 million.

*Ammonia*—modifications of Nessler's reagent; *e.g.*, see S. S. Graves, J. Am. Chem. Soc., 1915, 37, 1171. Useful in Kjeldahl nitrogen determinations. Will detect 1 part of ammonia in 160 million of water.

*Calcium*—calcium soaps are produced by ammonium stearate or by sodium sulphorincinate. Sensitiveness, about 1 in 5 million. Used in tests on blood, milk, water, etc.

*Chlorine*—cloud produced by silver chloride. In dangerous "war gases" a few thousandths of a milligram can be quantitatively estimated. (See A. B. Lamb, Carleton and Meldrum, J. Am. Chem. Soc., 1920, 42, 251.)

*"Mustard Gas"* (Dichlorodiethyl Sulphide)—an orange-red suspension of selenium is formed when the vapor is passed into a 1% solution of  $\text{SeO}_2$  in 1:1 sulphuric acid. As little as 0.005 mg. of "mustard gas" can be thus detected.

For further particulars and details, see "Photometric Chemical Analysis" by Prof. John H. Yoe (University of Virginia), 1928 (Wiley & Sons), and his two papers in Alexander's "Colloid Chemistry," Vol. II, Chem. Cat. Co., 1928; also Snell and Snell, "Colorimetric Methods of Analysis," D. Van Nostrand Co., 1936.

*Chromatographic Analysis* involves the simultaneous adsorption and separation of mixtures of organic compounds in solution, by such adsorbents as alumina, calcium hydroxide or carbonate, sugar, etc. When such a solution is allowed to percolate through a column of adsorbent, differences in the adsorbability of solutes results in the formation of a *chromatogram*, so called because with colored compounds zones of different color are visible, or may be made visible under ultraviolet light or by a suitable reagent. The chromatogram may be *developed* by washing with a suitable solvent, the several solutes moving down the column at different rates. The "developed" column may then be cut into sections, from each of which the purified adsorbate may be *eluted* (*i.e.*, desorbed) by another solvent. In some cases a slight

change in, or addition to a solvent will make it act as an elutor. Thus chromatograms formed by petroleum or benzene solutions of carotenoids yield the adsorbate to the same solvents containing a little alcohol. (See A. H. Cook, *Chemistry and Industry*, 1936, 55, 724-6, and the many references to literature there quoted.)

According to Zechmeister (*Annalen*, 1934, 509, 269) this method ranks with the application of spectrum analysis as a stimulus to research on natural coloring matters. It involves similar principles to those of F. Goppelshroeder's "*Capillary Analysis*" (*Anreung zum Studium der Capilläranalyse*," Basel, 1909; *Kolloidzeit.*, 1909). And in a paper entitled "Selective Adsorption and Differential Diffusion" (*J. Am. Chem. Soc.*, 1917, 39, 84-8) J. Alexander stated: "Not only may ions be thus separated, but if two solutes in the same solvent possess different rates of diffusion or different degrees of adsorbability, they also may be separated from each other by diffusion through a colloidal gel of septum . . . even when percolated through such a relatively coarse grained septum as sand, most solutions issue with a materially reduced content of solute, and benzopurpurin solutions may be thus decolorized."

## PHARMACY AND THERAPEUTICS

Those who laugh at curious Chinese remedies should glance at the illustrated section of the Chinese pharmacopeia, for the pictures of the hundreds of plants, etc., shown there speak in all languages. Recall to the scoffer that for over a thousand years, without knowing about "endocrines," Chinese physicians fed sheeps' thyroids to deficient children; to-day we use thyroid extract. Among their materia medica is the toad, distinguishable from the frog by the absence of webbing in its foot. Our own colonists used "toadskin ointment," and the use of the toad is often referred to in folk-lore. Thus in "As You Like It" Shakespeare says:

Sweet are the uses of adversity,  
Which, like the toad, ugly and venomous,  
Wears yet a precious jewel in his head.

Comparatively recently, Dr. John J. Abel showed that the skin of the toad *Bufo* contains adrenalin (an "endocrine" possess-

ing vaso-constrictor, styptic, and blood-pressure raising powers), as well as a substance he termed *bufagin*, which acts on the heart. Further studies have been made by H. Jensen and K. K. Chen; see *e.g.*, J. Bio. Chem. 1930, 87, 741-53.

Jenner introduced vaccination to Western medicine, but in a paper on "The Contributions of China to the Science and Art of Medicine," Dr. Edward H. Hume, of the College of Medicine, Yale-in-China, at Changsha, stated (Science, April 18, 1924): "Inoculation against small-pox was practised early, records being available of the transfer of virus from person to person in the 7th century, though the routine use of the method was not common until the 11th. A century before Jenner, the standard materia medica mentions the use of cow fleas for the prevention of small-pox." (It should here be noted that *insect transmission* is involved.)

In 1927 the Nobel prize was awarded to Dr. J. Wagner-Jauregg for his discovery that malarial infection may be used to combat certain nervous sequelae of syphilis. The former administrative officer of the Iramba tribe of "Tanganyika states" ("The Savage as Scientist," Ch. 7 in "Tales from the Outposts," Vol. XI, Blackwoods, 1933) that the medicine-man Mgendu came to urge that the chief Kinga, suffering from general paralysis, be moved from his kraal on the Daua plateau down to Sekenke in the Wembare Plains, one of the worst malarial districts in Africa. Said Mgendu: "The *vidudu* (mysterious insect-like things) of paralysis must fight with the *pilintu* (strange unknown worm-like things) so that the *pilintu* may be devoured; then must Kinga eat of the *nzizi chungu* (bitter roots), and he will be strengthened." The song of Chief Kitandu, dead four centuries, is still sung: "Do not build huts where mosquitoes live; for mosquitoes are evil, and make your blood hot."

The pharmacist and his predecessor, the iatrochemist, have long utilized colloid chemical processes. Mercury is readily brought into the colloidal state by trituration with fats (blue ointment) and was largely used by Paracelsus (1493-1540 [?]), though known long before. Gold was also thought to have great healing virtues, and its colloidal solutions were known. Eau-de-vie de Danzig seems to be a relic of this practice. It contains gold leaf. Thus Chaucer, in making a sly hit at the physician, says:

For gold in physic is a cordial;  
Therefore he loved gold in special.

On the other hand the poet, Pope, gives warning to pharmacists:

So modern 'pothecaries, taught the art  
By doctors' bills to play the doctor's part,  
Bold in the practise of mistaken rules,  
Prescribe, apply, and call their masters fools.

In making emulsions the pharmacist uses gum arabic, Irish moss, tragacanth, and the like. If ferric chloride be added to gum arabic emulsion of codliver oil, it coagulates the gum, and the oil, no longer protected by the emulsostatic action of the gum, promptly separates out. Milk of magnesia may be kept in colloidal state by carbohydrate protectors.

Colloidal silver (collargol, argyrol, and the like) is an excellent germicide in many cases and a preventive of *ophthalmia neonatorum*. In China the bite of a mad dog was treated by rubbing the saliva out of the bite *with a silver spoon or coin*, which would, no doubt, give off silver ions, or colloidal silver or silver oxide. Colloidal sulphur, artificially prepared and as ichthyol (a fossil sulphur-containing fish product), is valuable in skin troubles. Colloidal mercury (hygrol, blue ointment, and the like) is largely used. The introduction of gum arabic into the normal saline solution injected intravenously in cases of bleeding and surgical shock has saved many lives (Bayliss and Starling, Univ. of London). It increases and maintains the blood pressure and viscosity. Ferric salts, especially the chloride which readily hydrolyzes into the hydrate, act as styptics by coagulating the blood colloids. Alum and antipyrine act similarly.

On the other hand, citrates, oxalates, and hirudin (extracted from the head of the leech) tend to inhibit the coagulation of blood.

## ANTISEPTICS AND GERMICIDES

Colloid-chemical factors enter largely into the action of antiseptics, germicides and disinfectants.\* Before any such agent

\* See H. Bechhold, "Colloids in Biology and Medicine," trans. by J. G. M. Bullowa; E. K. Rideal, 5th Report on Colloids, etc., Brit. Assoc. Adv. Sci. 1923. I. S. Falk, Abstr. Bact., 1923, also Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied."

can be effective against an organism, it must reach and be adsorbed by the organism. Flocculation of the bacteria may then follow. This recalls the effect of typhoid antitoxin shown in the Widal test, where a subsequent lysis or solution of the typhoid bacillus occurs. Or the antiseptic may then enter the germ, and temporarily or permanently inhibit its internal catalysts. In the latter case the agent may be justly called a germicide; but in some cases the bacteria, or their more resistant spores, resume their life processes again as soon as the disinfectant is removed by washing or by diffusion. Dilution may remove an antiseptic before its action becomes irreversible.

Where bacteria are hidden in narrow clefts, a low surface tension of the antiseptic solution may be aidful in permitting penetration of the fluid, and the "wetting" of the germ so that adsorption can take place. Sodium chloride increases the effectiveness of phenol (carbolic acid), an effect analogous to the "driving-on" action of salts in dyeing. Rideal attributes the selectiveness of adsorption to the sub-microscopic inhomogeneity of the external bacterial surface, which has a checker-work of acid and basic areas.

Since bacteria are of the order of size of  $1\ \mu$ , their motion is partially Brownian, though the unequal liberation both of gas and diffusing products is also a factor. As Albert Mary\* has shown (*Dictionnaire de Biologie Physiciste*, 1921) the tuberculosis bacterium (Koch's bacillus) may become toxic by the selective adsorption of substances normally present in small amount in the blood (possibly sterols, etc.). The extreme sensitiveness of bacteria to minute changes in acidity (pH) shows how intimately their life is controlled by variations in the degree of swelling or dispersion or electrical charge of their constituent colloids. Besides, bacteria often surround themselves with a coat or capsule, which protects them. This capsule is often of carbohydrate nature (M. Heidelberger, Rockefeller Inst. for Med. Res.), and if the capsule is digested off by a suitable enzyme, the phagocytes can then envelop and digest the bacterium (Avery and Dubos, Rockefeller Inst. for Med. Res.).

The practical behavior of an antiseptic or germicide may be greatly influenced by substances incidently present in the material

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\* See his paper in Alexander's *Colloid Chemistry, Theoretical and Applied*, Vol. II (1928).

to which it is applied. For example, when the Prohibition law was in effect here, officers raided a brewery and took sample bottles of the brew. Into each bottle they dropped a "poison tablet," later identified by the Government chemist as containing bichloride of mercury; and the bottles, when tested nine days later, each showed more than the legally permitted  $\frac{1}{2}$  per cent of alcohol. Cross examination of the chemist elicited that the common antidotes for bichloride of mercury poisoning are milk, white of eggs, and similar protein-containing substances, which form insoluble mercury "proteinates"; and also that beer contains proteins. It was then pointed out that each of the bottles contained a considerable precipitate, and that some of them were actually fermenting when they were produced in evidence. The Judge immediately adjourned the trial and ordered a re-test of each of the samples. Where alcoholic fermentation had proceeded, the alcoholic content had risen; where acetic fermentation had supervened, the alcohol dropped—the beer had turned "sour." Consequently no one could tell what had been the alcoholic content *at the time of seizure*, nine days before the first test. The choice of a suitable antiseptic would have obviated this dilemma.

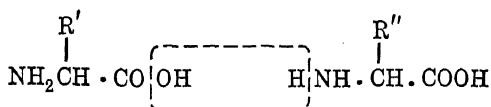
## CHAPTER XVII

### PROTEINS AND CARBOHYDRATES

#### PROTEINS

IT HAS long been known that on hydrolytic breakdown natural proteins, *e.g.*, albumin, gelatin, yield  $\alpha$ -amino acids, that is, amino acids in which an  $\text{NH}_2$  group immediately adjoins the  $\text{COOH}$  group. The simplest amino-acid is glycine or glycoll. Prof. Emil Fischer (University of Berlin) who so greatly advanced our knowledge of protein and carbohydrate chemistry, was able to synthesize an octadecapeptide, that is, a molecule built up of 18  $\alpha$ -amino acid molecules; but these were all the comparatively simple  $\alpha$ -amino acids, glycine and leucine. To indicate how far even this 18 molecule complex is from a natural protein, there are listed on page 295 the various  $\alpha$ -amino acids and similar derivatives isolated from hydrolyzed gelatin.

Fischer's work indicated that the linkage of amino acids to form larger molecules involves a dehydration according to the scheme first suggested by Hofmeister:



Proteins are amphoteric, that is, they combine with and neutralize both acids and bases. They are therefore termed *amphotelytes*. This property used to be explained by assuming that their amino acids are un-ionized in solution; that added acids give an  $\text{H}^+$  to the  $\text{NH}_2$  group, to form an  $\text{NH}_3^+$  ion, while bases take an  $\text{H}^+$  from the  $\text{COOH}$  group, to form a  $\text{COO}^-$  ion.

N. Bjerrum (*Z. physikal. Chem.* 1923, 104, 147) suggested that in pure aqueous solutions amino acids of the fatty acid series are completely ionized, yielding a chameleon-like *amphoteric ion*, generally called a *zwitter-ion*, the German name originally suggested, meaning an hermaphroditic, mongrel or hybrid ion. Acids drive back the ionization of the  $\text{COOH}$  arm; bases, that of the  $\text{NH}_2$  arm of the two-fisted zwitter-ion.

TABLE XXIV. COMPONENTS OF GELATIN  
(Dakin's analysis)

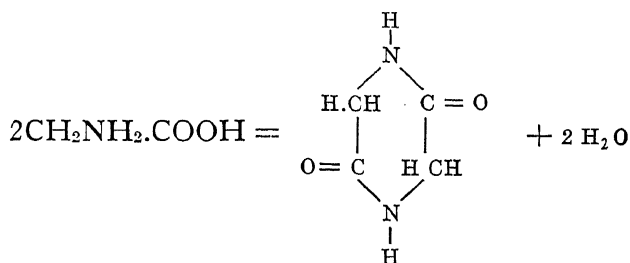
<i>Mono-amino mono-carboxylic Acids</i>	Per cent.
Glycine ( $\alpha$ -amino-acetic acid, $\text{CH}_2 \text{NH}_2\text{COOH}$ )	25
Alanine ( $d$ - $\alpha$ -amino-propionic acid, $\text{CH}_3\text{CHNH}_2\text{COOH}$ )	8.7
Leucine ( $l$ - $\beta$ -dimethyl- $\alpha$ -aminobutyric acid, $(\text{CH}_3)_2\text{CH}.\text{CH}_2.\text{CHNH}_2\text{COOH}$ )	7.1
Phenylalanine ( $l$ - $\beta$ -phenyl- $\alpha$ -aminopropionic acid, $\text{C}_6\text{H}_5.\text{CH}_2.\text{CHNH}_2\text{COOH}$ )	1.4
Tyrosine ( $l$ - $p$ -hydroxyalanine— $\text{C}_6\text{H}_4\text{OH}.\text{CH}_2.\text{CHNH}_2\text{COOH}$ )	0.01
Serine ( $l$ - $\beta$ -hydroxy- $\alpha$ -amino propionic acid, $\text{CH}_2\text{OH}.\text{CHNH}_2\text{COOH}$ )	0.4
<i>Diamino-mono-carboxylic Acids</i>	
Lysine ( $\epsilon$ - $\alpha$ diamino-caproic acid $\text{CH}_2\text{NH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2\text{COOH}$ )	5.3
Arginine ( $d$ - $\delta$ guanidine amino-valeric acid, $\begin{array}{c} \text{NH} \\ \parallel \\ \text{C} - \text{NH} \text{CH}_2.\text{CH}_2.\text{CH}_2.\text{CH}_2.\text{NH}_2\text{COOH} \\ \parallel \\ \text{NH}_2 \end{array}$	8.2
Histidine ( $l$ - $\beta$ imidazole- $\alpha$ -aminopropionic acid $\begin{array}{c} \text{CH} \\ \diagup \quad \diagdown \\ \text{HN} \quad \text{N} \\   \quad   \\ \text{HC} = \text{C} . \text{CH}_2 . \text{CH} \text{NH}_2 . \text{COOH} \end{array}$	0.9
<i>Mono-amino-dicarboxylic Acids.</i>	
Aspartic Acid ( $l$ - $\alpha$ -aminosuccinic acid $\text{COOH}.\text{CH}_2.\text{CH} \text{NH}_2.\text{COOH}$ )	3.4
Glutaminic Acid ( $d$ - $\alpha$ -amino glutaric acid $\text{COOH}.\text{CH}_2.\text{CH} \text{NH}_2.\text{COOH}$ )	5.8
<i>Imino Acids</i>	
Proline $\begin{array}{c} \text{H}_2\text{C} - \text{CH}_2 \\   \\ \text{H}_2\text{C} \quad \text{C} . \text{COOH} \\   \\ \text{NH} \end{array}$	9.5*
Hydroxyproline $\begin{array}{c} \text{OH} . \text{HC} - \text{CH}_2 \\   \\ \text{H}_2\text{C} \quad \text{C} . \text{COOH} \\   \\ \text{NH} \end{array}$	14.1

\* Bergmann found 2.0 in the sample of gelatin he analyzed (J. Biol. Chem. 1935, 110, 471). D. D. Van Slyke has also reported the presence of a base not yet identified.

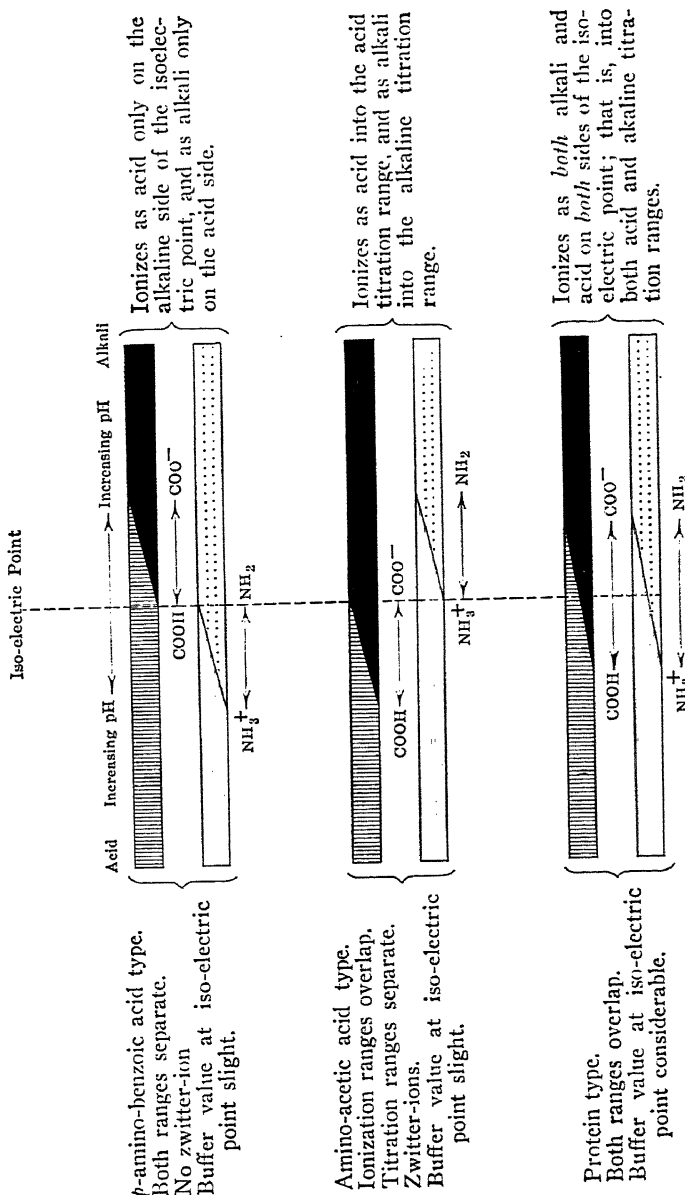


The following diagram, Fig. 20, adapted from Dr. Dorothy Jordan Lloyd (J. Int. Soc. Leather Trades' Chemists, Apr., 1933, pp. 245-58; see also Trans. Farad. Soc., 1935, 31, 317-324) indicates why all ampholytes do not form zwitter-ions. As pointed out on p. 31, the *ionizable* and the *titratable* acidity (or alkalinity) are not always identical. Where the ionization *and* titration ranges of the acid and the basic groups of an ampholyte are quite *separate*, no zwitter-ions appear. This is the case with *p*-amino-benzoic acid. With amino-acetic acid (glycine) however, although the ionization ranges are separate, the titration ranges overlap, and the zwitter-ion effect comes into evidence. With proteins both ranges overlap, probably because their complicated structure comprises many amino acids with different isoelectric points; and this is responsible for the rather large buffer value proteins show at their iso-electric points.

The x-ray evidence (see *e.g.*, W. T. Astbury and R. Lomax, J. Soc. Chem. Ind., 1934, 53, 979, J. Chem. Soc., 1935, 846-51) confirms the view that protein molecules have an elongated body or "backbone" of amino acids linked by peptide bonds of primary valency. From this body project the large number of incidental side-chains, whose mutual attractions may force the long body into spiral or other contortions, or may bind the fibrils sidewise into fibers or fiber-like bundles. Ring structures may also exist. Thus it is possible to condense two molecules of glycine to form 2, 5-diketopiperazine



It seems likely, however, that closed rings predominate, which limits the coordination to the side chains. D. Jordan Lloyd and T. Moran (Proc. Roy. Soc., London, 1934, A 147, 382-95) found that 1 gram of highly purified dry gelatin carries 0.5 gram of closely bound water, indicating that a molecule of gelatin (mol. wt. 34,500) is closely bound to about 960 water molecules, a



\* The Iso-electric point is not the same for all proteins

Fig. 20.

figure approximating the calculated number of possible co-ordination centers. They regard the whole of the water to be in chemical combination with the protein and state:

"The hydration of proteins can occur by the formation of a coordinate link between a water molecule and certain groups in the protein structure; for instance, the positively charged basic groups of the proteins readily accept a pair of electrons from the oxygen of a water molecule on to one (or more) of the hydrogen atoms.

"Conversely, the negatively charged acidic groups of the proteins readily donate a pair of electrons from the singly bound oxygen atom to the hydrogen of the water molecule.

"Neutral groups, such as OH, NH<sub>2</sub>, NH, COOH, can similarly form coordinate links with water molecules either by the donation or the acceptance of a pair of electrons. The formation of a coordinate link would be expected to show the usual characteristics of chemical change, namely, heat changes (commonly evolution of heat) and considerable resistance to changes in physical conditions such as temperature, etc. It should be noticed, however, that there is no way of constructing a co-ordinate link between a protein molecule and a water molecule except by donating a pair of electrons on to a chemically combined hydrogen atom. Since this already carries two electrons in its sheath, and is in a stable condition, the link formed by making an outer sheath of four electrons will not be very resistant if compared with those links where the donation of two electrons leads to the completion of an electron sheath. Water co-ordinately bound to the protein molecule would be expected to show a considerable but not extreme resistance to, say, the forces of evaporation. Katz's data on the vapour pressure isotherm of a gelatin gel show that this is actually the case."

As previously pointed out, it is a matter of opinion as to whether co-ordinately bound water shall be considered as chemically or physically bound (see pp. 23 and 26). Gelatin super-dried at about 120°, becomes insoluble, like ossein, indicating that too close an approach of particles (molecules, or their chains or arms) creates bonds which the presence of water cannot loosen again. (See further on p. 301.) Heat changes accompany the adsorption of gases by carbon, and water of crystallization is not regarded as chemically bound by most chemists.

Some indication of the structural complexity of a protein is given by the calculations of Atkin (J. Int. Soc. Leather Trades Chemists, 1933, 17, 575) that the gelatin molecule (atomic weight 34,500) is formed by the condensation of 360 amino-acid residues, having about 200 points on the side chains capable of fixing water by co-ordinate linkage. If the carbonyl [CO] and amino groups of the condensed amino acid residues of the molecular "backbone" are in open form, they offer about 700 possible co-ordination points additional to the 200 mentioned. Since proteins differ in ultimate chemical nature, depending on their source, a protein "salt" or a "proteinate" must generally be regarded as a mixture of chemical compounds, even if true chemical compound formation be assumed with each chemical individual in the assemblage.

The remarkable work of Prof. The Svedberg and his collaborators (see p. 137) has shown that many proteins are *poly-disperse*, that is, in solution they have more than one kind of molecule, and the number often changes with changing pH. Thus the blood pigment hemocyanin from the snail (*Helix*), at the alkaline stability limit, in addition to unchanged molecules of atomic weight 6,600,000, shows two dissociation products of  $\frac{1}{2}$  and  $\frac{1}{8}$  of this value, respectively. But hemocyanin from the king crab (*Limulus*, generally called the horse-shoe crab), shows, at its isoelectric point, four components with molecular weights of 3,300,000, 1,600,000, 400,000, and 100,000, indicating masses in the proportion  $1:\frac{1}{2}:\frac{1}{8}:1/32$ . The molecules of natural proteins appear to be built up of units of molecular weight 34,900, but only about a dozen of the many possible multiples are known, as appears from Table XXV in which are given some of the results of Svedberg \* and his pupils, together with some other data.

The X-ray studies of Astbury and Lomax (*loc. cit.*), indicates that a fully-extended polypeptide chain, *e.g.*, in the keratin of mammalian hairs, has two principal side-spacings roughly at right angles with each other, one (about 4.5 Å.) representing the effective thickness of the "backbone" of the chain, the other (about 10 Å.) representing the average lateral extension of the side-chains jutting out from the amino-acid residues. When steam acts on hair, the swelling appears to be almost exclusively asso-

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\* Sincere thanks are due to Prof. Svedberg for his kindness in revising this table so as to include his most recent results.

TABLE XXV

Protein	Molecular weight (determ.)	Molecular weight (calc.)	Sedim. const. $\times 10^{13}$	Isoelectric point pH
Erythrocrucorin (clam blood)	33,600	$1 \times 34,900$	3.46	.....
Lactoglobulin (cow's milk)	35,900		3.14	5.19
Pepsin (gastric juice)	37,300		3.3	.....
Insulin (pancreas)	35,100		3.47	.....
Egg Albumin (hen's egg)	42,100		3.55	4.58
Hemoglobin (horse blood)	68,500	$2 \times 34,900 = 69,800$	4.5	6.93
Serum Albumin (horse blood)	67,000		4.5	4.80
Serum Globulin (horse blood)	150,000	$4 \times 34,900 = 139,600$	7.1	.....
Phycoerythrin (red algae)	291,000	$8 \times 34,900 = 279,200$	12.0	4.25
Phycocyan (red algae)	279,000		11.7	4.85
Edestin (hemp seed)	303,000		12.8	5.5
Excelsin (brazil nut)	294,000		13.3	.....
Amandin (almond)	329,000		12.5	.....
Hemocyanin (spiny lobster blood)	453,000	$12 \times 34,900 = 418,800$	16.4	.....
Hemocyanin (deep-water prawn)	397,000		17.4	.....
Hemocyanin (lobster blood)	768,000	$24 \times 34,900 = 837,600$	22.6	4.95
Erythrocrucorin ( <i>Planorbis</i> snail blood)	1,587,000	$48 \times 34,900 = 1,675,200$	33.7	4.77
Hemocyanin ( <i>Calocaris</i> crayfish blood)	1,327,000		34.0	.....
Erythrocrucorin (sand worm blood)	3,000,000	$96 \times 34,900 = 3,350,000$	57.4	4.56
Hemocyanin (squid blood)	3,316,000		56.2	.....
Erythrocrucorin (earth-worm blood)	3,068,000		60.9	5.28
Hemocyanin (French snail blood)	6,668,000	$192 \times 34,900 = 6,660,000$	98.9	5.05
Hemocyanin (conch blood)	9,660,000	$288 \times 34,900 = 9,900,000$	126.2	4.49

ciated with enlargement of the wider side-spacing. Collagen and gelatin show similar well-marked spreading of the "side-chain spacing" when, on simple soaking, water penetrates between the long chains. All this is comprehensible in view of the great variation of atomic and molecular forces with small changes in distance. (See p. 86.) Similar space-changes were observed in comparative X-ray photographs of egg- and serum-albumins (both raw and denatured), pepsin, trypsin, zein (from maize),

casein, globulins from squash and tobacco seeds, and edestin from hemp seed, following their absorption of water, or of alcohol vapor in the case of zein which is not soluble in water though it dissolves in alcohol. On second examination at a later time, the specimen of pepsin gave a new photograph which reverted to the original on drying.

All the proteins examined seemed to have the typical backbone and side-chain structure first identified in fibers, and fall into an "order of crystallinity," tobacco seed globulin being highest with *eight* well-defined rings in the X-ray spectrogram. Svedberg's recent analysis also indicates *eight* times the basic protein "unit" for the molecular weight of the seed globulins.

#### PHYSICO-CHEMICAL CHANGES IN PROTEINS— DENATURATION

Graham referred to the colloidal state as *dynamical*, that is, a state fraught with change. Entirely apart from the ultimate chemical structure of a protein, we must consider not only what the colloidal condition of the protein *now is*, but also what it *has been* and what it *may become*, in consequence of changes in the mode of assemblage of its molecular units.

Changes in solubility and gross physical behavior (*e.g.*, the "curl," stretching and shortening of hair, feathers, horn, textile fibers, muscle) are produced or catalyzed in proteins by heat, drying, pressure, radiation, and a wide variety of chemical agents, such as acids, alkalis, urea, acetone, alcohol, iodides, salicylates, thiocyanates. The salts mentioned seem to cause loosening of the bonds responsible for the intermolecular arrangement, because their solutions soften or dissolve gelatin and other proteins. Tablets of such salts should not be swallowed because of the possible damage they may do to the wall of the stomach. Dilute solutions should be taken, and instructions to this effect are generally found on bottles of bromide tablets.

Such changes, if sufficiently marked, have been generally termed *denaturation*; they are reversible if not carried beyond critical limits. Since denaturation represents no one clear-cut change, the conditions whereby it has been accomplished should always be stated (C. L. A. Schmidt, in Harrow and Sherwin's "Textbook of Biochemistry," 1935, p. 232). Prof. Wilder D. Bancroft (Cornell University) and J. E. Rutzler, Jr., after dis-

cusssing the denaturation of albumin (J. Phys. Chem., 1931, 35, 144), even suggest that the term "denaturation" be dropped as a "myth"; they confirmed the view of Prof. Mona Spiegel-Adolph (Temple University, Alexander's Colloid Chemistry, Vol. II, 303-26), that the process is reversible, and found that native and denatured albumin produced the same antibodies (see p. 416).

The commonest denaturation phenomenon is the setting of egg white on heating; but Prof. P. W. Bridgman (Harvard University) showed that it can be coagulated by high pressure alone. Hemoglobin, when denatured by salicylates, becomes subject to attack by trypsin and shows an altered absorption spectrum, identical with that shown by "parahematin" and also by solutions of hematin in pyridine. (Anson and Mirsky, J. Gen. Physiol., 1931, 14, 605; 1934, 17, 393-9; J. Phys. Chem., 1931, 35, 185). The potency of the effects produced on the behavior of proteins in denaturation experiments by traces of salts, led Prof. Wolfgang Pauli (University of Vienna) to state that "the same pH with or without the presence of salt can mean something entirely different relative to the condition of the protein." (Ann. Rev. of Biochem., 1934, p. 118.) Solutions of *dialyzed* egg albumin, when heated to 100° or treated with alcohol, show no visible effect, but on addition of a trace of electrolyte a copious white flocculate immediately appears. This fact must be borne in mind when considering the "precipitin" reactions of immunology (see p. 415).

Prof. W. T. Astbury\* and R. Lomax (University of Leeds) have made extensive X-ray investigation of the alteration in molecular and micellar relationships (that is, the colloidal changes) induced by subjecting proteins to physical and mechanical influences, many of which had been used to produce denaturation. (J. Chem. Soc., 1935, 946-51.) They found that as we proceed downward in the following series of X-ray powder photographs of proteins, taken *at atmospheric humidity*, the X-ray reflections become both fewer and more diffuse, indicating a descending order of "crystallinity":

Tobacco-seed globulin  
Squash-seed globulin  
Edestin, from hemp seed

\* Thanks are due to Prof. Astbury for his kindness in supplying reprints.

Boiled egg-white  
Pepsin  
Ordinary egg-white  
Casein  
Zein

They conclude that by denaturation a protein is forced in the direction of crystallinity, being moved upward in the "crystalline series." "Before denaturation, the peptide chains of the protein molecule seem to be clinging together chiefly by way of their side-chains, but after denaturation, this interaction is consolidated by marked coalescence of the main-chains by way of the backbone linkages also . . . the completely denatured state is that in which the peptide chains have been freed from any specific configuration and aggregated into regular bundles, or crystallites, held together by two principal linkages, the backbone and side-chain linkages . . ."

This leads to the view that "the fibrous proteins, such as fibroin, gelatin, keratin, and myosin (Boehm and Weber, *Kolloid Zeit.*, 1932, 61, 269; Astbury and Dickinson, *Nature*, 1935, 135, 95), may all be looked upon as either in a state of denaturation, or configurationally disposed towards such a state. Fibroin and keratin are very insoluble proteins, and so is myosin when once it has been thoroughly dried, and even gelatin becomes progressively more insoluble on standing. At all events, we appear to have a significant analogy between these characteristically stable proteins and non-fibrous proteins which have been brought into a stable and resistant state by one or the other methods of denaturation."

Astbury and W. A. Sisson (*Proc. Roy. Soc., London*, 1935, 150, 533-51) state that all proteins, in the molecular sense, are either actually or potentially fibrous. They find that when keratin (hair, horn, nail, whalebone, porcupine quill) is swollen by soaking or by steaming, mechanical pressure or "ironing" flattens out the normal "crimped" molecular structure ( $\alpha$ -keratin) into an extended form ( $\beta$ -keratin), a flat "polypeptide grid" where the fully extended main-chains are bound sidewise through electrostatic and co-valent linkages between certain of their side-chains. In  $\beta$ -keratin crystallites we have superimposed "grids," the main-chains being parallel and piled up about 4.65 Å. apart. The normal equilibrium form,  $\alpha$ -keratin, appears to arise from



the  $\beta$ -form by regular folding or buckling of the main-chains lengthwise, that is, in planes transverse to the side-chains, which are thereby brought closer together (from about 3.4 Å. to 1.7 Å.). In both the flat and the folded "grids," the main-chains remain about 9.8 Å. apart. Astbury estimates the width of the keratin crystallites in the direction of the side-chains to be about 100 Å. (10 chain-widths). This is based on a correlation of X-ray with swelling data (Trans. Faraday Soc., 1933, 29, 193). Speakman (Proc. Roy. Soc., 1931, A, 132, 167), from swelling data alone, estimates an average thickness of 200 Å. for the micelles.

Various processes for producing "permanent waves" in human hair must be considered in the light of these disclosures, as well as the "pressing" of woolen clothing.

Astbury and Lomax (*loc. cit.*) point out that the molecular rearrangement involved in the  $\alpha$  to  $\beta$ -keratin transformation, or the reverse, depends on the presence of water, for "unless the active side-chains are solvated, they seize upon one another so strongly that the possibility of intramolecular movement is practically eliminated. Similar ideas also account satisfactorily for the well-known hysteresis between adsorption and desorption of water by proteins, while for stability to be maintained in regular aggregations (crystals) of 'globular' protein molecules we can imagine that it is essential for each molecule to be 'protected' from its neighbours by an intermolecular wrapping of water or some still more specific reagent. Once the system of protective molecules becomes inadequate, *e.g.*, owing to evaporation, neighboring protein molecules may powerfully disturb or actually destroy one another, with the result that their constituent peptide chains are liberated to recrystallize by simple parallel alignment. . . ."

All this accords with the long standing view of colloid chemists as to the protective action of water. Barus and Schneider (Zeit. phys. Chem., 1891, 8, 297) assumed the existence of aqueous envelopes in colloidal silver, and Zsigmondy ("Colloids and the Ultramicroscope," 1909, pp. 175-181) discussed the "protective action of water" on metal hydrosols. Hofmeister stated that gelatin can be reconverted into collagen by heating it to 130°, and supposed that this indicates that collagen is an anhydride of gelatin. J. Alexander stated: "It is extremely

doubtful if collagen is regenerated under these conditions, the more probable explanation being that, upon driving off the water, the constituent particles of the gelatin approach so close as to form an irreversible gel, thus rendering it insoluble." (Allen's Commercial Organic Analysis, 4th ed., 1916, Vol. 8, p. 586, 5th ed., Vol. 10, p. 127; also "Glue and Gelatin," 1923, p. 115.) In view of the facts with cellulose and starch, discussed further on, it may well be that in proteins evidence will still be found of the existence of protective films of "impurities" which act as *cohesive colloids* (see p. 322), binding the protected units together.

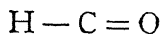
Bernal and Crowfoot (Nature, 1934, 133, 794) examined with X-rays some of the active crystalline pepsin prepared by Dr. J. H. Northrup (Rockefeller Inst. for Med. Research; J. Gen. Physiol., 1930, 13, 739; 1934, 16, 267), and report that, *when examined in their mother liquor*, the crystals appear to consist of oblate spherical molecules 25 to 35 Å. in diameter, arranged in hexagonal nets, which are related to each other by a hexagonal screw-axis. Svedberg's pupils, Philpot and Erickson-Quesnel (Nature, 1933, 132, 932) calculated that pepsin in solution has roughly spherical molecules. Examination of crystalline insulin warranted similar conclusions (Crowfoot, Nature, 1935, 135, 591). On the other hand, Astbury and Lomax (*loc. cit.*) found that pepsin can give a variety of X-ray patterns, depending whether it is highly dried, or at atmospheric humidity, or wet, and believe that most so-called protein "crystals" in the dry state are probably only pseudomorphs after partial or complete denaturation. They envisage three stages in the life of a non-fibrous protein: (1) the "specific" stage, in which the protein is truly itself; (2) the "denatured" stage, in which its delicately balanced configuration has been disintegrated sufficiently to release or even to build up peptide chains; (3) the "coagulated" stage, where these chains have aggregated into regular parallel bundles or crystallites, analogous to those of the fibrous proteins.

Dr. Dorothy Jordan Lloyd ("Chemistry of the Proteins," 1926, Chapter 13), discusses denaturation and coagulation at length. She states that coagulation is a physical condition, and by suitable means the coagula may be redispersed or dissolved; but denaturation involves an irreversible chemical change (W. B. Hardy, 1899), such as may perhaps exist in the heated dialyzed

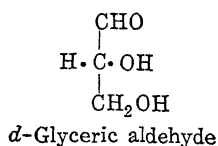
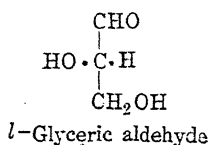
albumin, above referred to, if co-valent linkages are broken. "If two peptide chains were originally bound together by sharing cystine residues, hydrolytic breakdown of the —S—S— linkages would lead to the appearance of —SH groups (cf. Harris, Proc. Roy. Soc., 1923, B, 94, 426; Speakman, Nature, 1933, 132, 930)." (Astbury and Lomax.)

### CARBOHYDRATES

The empirical formulae of the simple carbohydrates (termed *monosaccharides*) are multiples of  $\text{CH}_2\text{O}$  which also represents formaldehyde, a substance theoretically formed in plants by catalytic reduction of  $\text{CO}_2$ , prone to polymerization, and thus a precursor of carbohydrates.

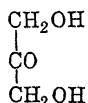


Glycollic aldehyde,  $\text{H}_2 - \text{C} - \text{OH}$ , is based on 2  $\text{CH}_2\text{O}$  and is called *diose*. Having no asymmetric carbon atom, it is optically inactive. Since all natural sugars are optically active, the *triose* (3  $\text{CH}_2\text{O}$ ) glyceric aldehyde is justly regarded as the simplest sugar, its dextro- and levorotatory forms being diagrammatically represented thus:



Sugars based on 4  $\text{CH}_2\text{O}$  (4 C atoms) are termed *tetroses*; on 5  $\text{CH}_2\text{O}$  (5 C atoms), *pentoses*; on 6  $\text{CH}_2\text{O}$  (6 C atoms), *hexoses*, etc.

A further complication in the chemistry of the carbohydrate molecule arises from the fact that sugars of the aldehydic form (*aldoses*) may by isomeric change assume ketonic or keto form (*ketoses*). Thus both *d*- and *l*-glyceric aldehyde could pass over into

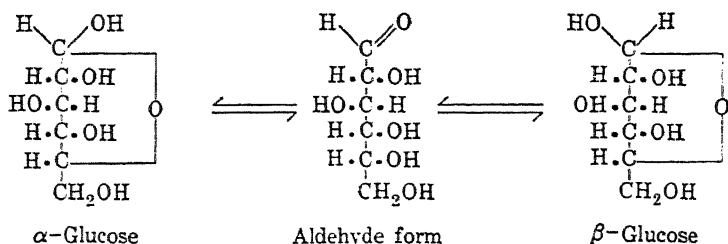


Dihydroxyacetone

The four different groups about an asymmetric carbon atom may be assembled either clockwise, or counter-clockwise, giving forms that are mirror pictures of each other (*stereo-isomers*). As van't Hoff pointed out, sugars with  $n$  asymmetric carbon atoms generally have  $2^n$  possible stereo-isomers; so that ordinary *d*-glucose (a aldehydic hexose) has 16 possible stereo-isomers. In general the sugars are very reactive; they may be oxidized, reduced, and condensed with other substances; and they form esters, ethers, addition compounds, etc. (For further details, see Harrow and Sherwin's "Textbook of Biochemistry," Chapt. II by R. S. Tipson and E. T. Stiller.)

As Prof. E. Frankland Armstrong observes ("The Simple Carbohydrates and the Glucosides," 3rd ed., 1919, p. 1), the carbohydrates, together with the proteins, are of premier importance among organic compounds, because of the important rôle they play, in plants and animals, in functional activity and structural form. Since glucose is the ubiquitous plant carbohydrate and the parent substance of cane sugar, maltose, starch, and cellulose, besides being the chief carbohydrate burned in the animal organism, we must here concentrate mainly on glucose and its derivatives.

*The Heterocyclic or Ring Structure of Sugars.* The straight-chain structure of the sugars, with an aldehydic CHO terminal group in the case of aldoses, is now supposed to exist only as a transient phase in an equilibrium between the  $\alpha$  and  $\beta$  forms indicated as follows:

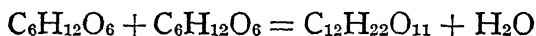


It will be noted that the oxygen bridge, or lactone ring, as it is called, joins the *first with the fifth or  $\delta$  carbon atom*; and this

is the case in the more stable form of the glucoses, which are labeled  $\delta$ -lactones. However, still other but less stable forms have been prepared, in which the oxygen bridge links the first with the fourth or  $\gamma$  carbon atom of the chain. On long standing or heating to  $66^\circ$ , the  $\gamma$  sugar derivatives pass over into the  $\delta$  forms.

In 1927 Prof. W. N. Haworth \* (University of Birmingham), who has done outstanding work in this field, proposed a great simplification of the cumbersome and conflicting forms of nomenclature which had arisen as more and more facts regarding the structural complications of the sugars were elicited by research. Normal sugars with the 1-5 lactone ring were considered as arising from *pyran* and termed *pyranoses*, while those with the 1-4 lactone ring were considered as based on *furan* and termed *furanoses*. Haworth's nomenclature has been generally adopted,† and in the illustrations of its application given below use is made of the flat ring structure warranted by the extensive X-ray spectrophotographic evidence, which supplements and extends the splendid chemical work. (See Figs. 21-22, pp. 309-310.)

This nomenclature transcends the academic interest it would have if it concerned merely the crystalline sugars of the pentose and hexose series, which are ordinarily accessible in free isolated state. But these simple sugars acquire wider significance as the building blocks from which are formed the complex natural carbohydrates—*disaccharides* such as maltose, sucrose and cellobiose, and the relation of these to such *polysaccharides* as starch, cellulose, inulin, etc. Thus the equation of earlier days



indicates merely that two hexose molecules or residues have united to form a disaccharide, with the elimination of a molecule of water. The following illustrations, after Haworth, show how much more precise and useful is the more recent structural knowledge. Two  $\alpha$ -glucopyranose molecules combine, with the

\* Prof. Haworth has kindly supplied reprints and given permission to reproduce his splendid illustrations, copies of which were supplied through the courtesy of Dr. Miall, editor of "Chemistry and Industry."

† But not yet officially.

## Pyranose Forms of Sugars.

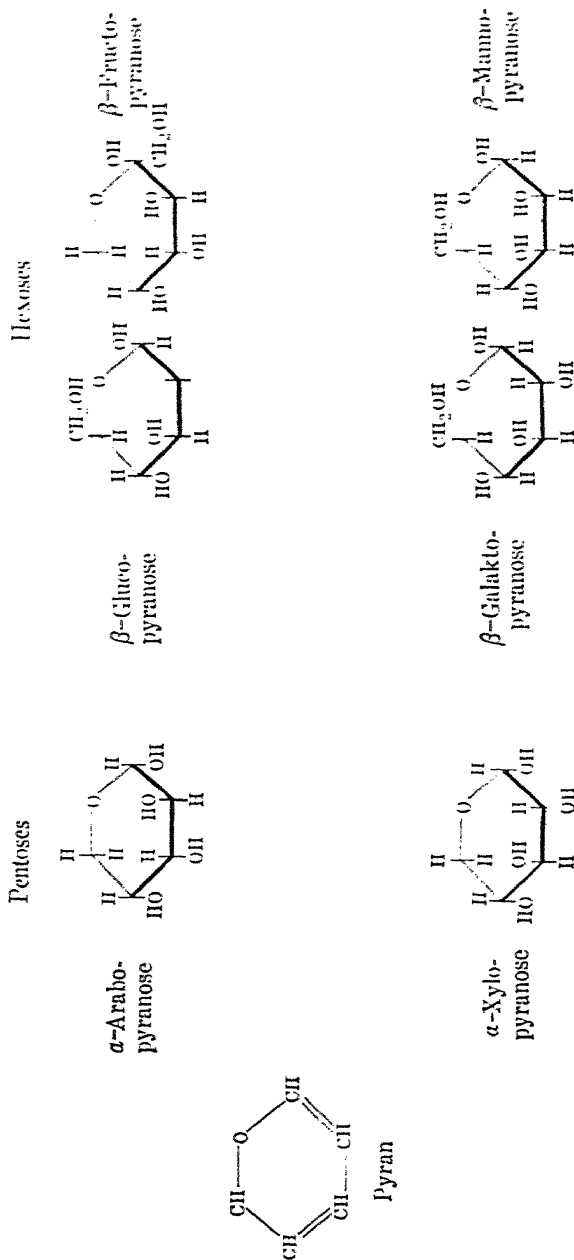
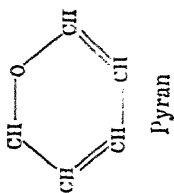
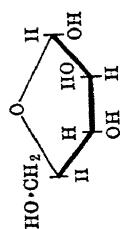
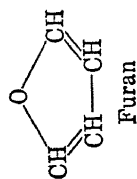


Fig. 21.



## Furanose Forms of Sugars.

Pentoses

 $\alpha$ -Arabinofuranose

Furan

Hexose

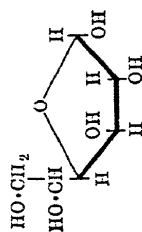
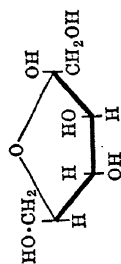
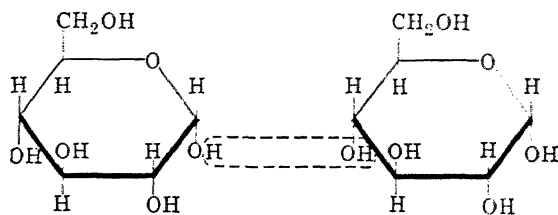
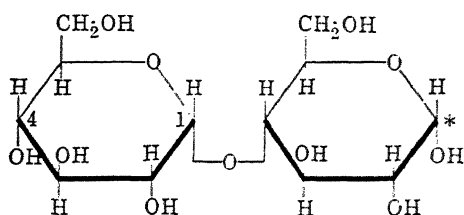
 $\alpha$ -Glucofuranose $\beta$ -Fructofuranose

Fig. 22.

elimination of water, to form one molecule of  $\alpha$ -maltose (the basis of starch) thus:



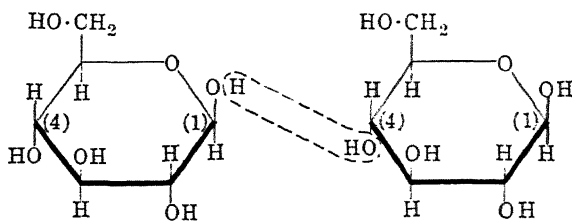
Union of two  $\alpha$ -Glucopyranose molecules



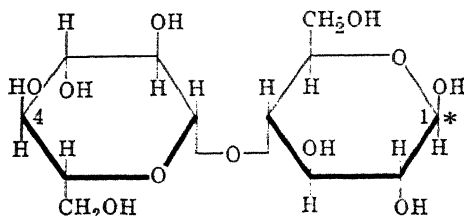
$\alpha$ -Maltose

Fig. 23.

Two glucopyranose molecules combine, with the elimination of water, to form one molecule of cellobiose (the basis of cellulose) thus:



Union of two  $\beta$ -Glucopyranose molecules



$\beta$ -Cellobiose

Fig. 24.



This last formulation shows the two  $\beta$ -glucopyranose molecules united through two OH groups, one of which lies above, and the other below the planes of their respective pyranose rings. Therefore one of the rings is inverted, in order to bring the final cellobiose formula into alignment. It is the simple spatial or stereoisometric difference illustrated that underlies the wide difference between starch, which is formulated on the maltose model, and cellulose, which is based on the formulation of cellobiose. Haworth illustrates this by the following diagrams:

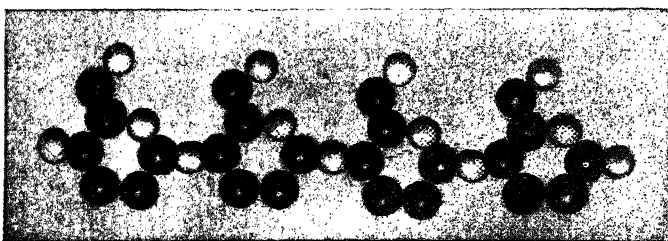


Fig. 25. Two maltose units, assembled as in starch.

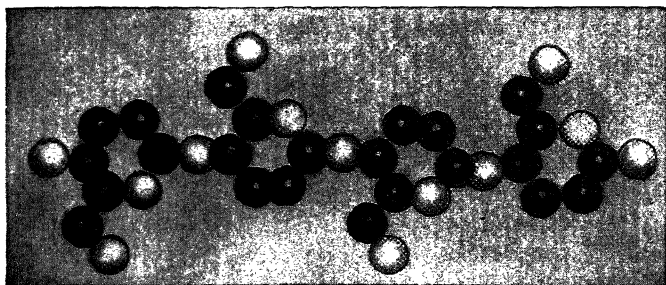


Fig. 26. Two cellobiose units, assembled as in cellulose.

*Sucrose*, the ordinary cane or beet sugar of commerce, represents another type, a molecule of  $\alpha$ -glucopyranose being linked with a molecule of  $\beta$ -fructofuranose, through sharing a common oxygen atom or glucosidic link situated at the first carbon atom in each of these two hexoses. (Fig. 27.)

The fructose residue, as established in the biose sucrose, also occurs in the polysaccharides inulin from *Compositae* (e.g., dahlia), and levan from grass.

The X-ray diagram of native cellulose (Fig. 28) fits perfectly the cellobiose picture determined by the classical constitutional methods of organic chemistry, and reflects the symmetry of the cellobiose chain in which the sixth carbon atom (or side chain) of each hexose residue is alternately above and below the plane of the rings. The maltose chains of starch, with the sixth carbon atom chains all on one side, giving a model departing materially, in zig-zag or spiral fashion, from the comparatively straight line

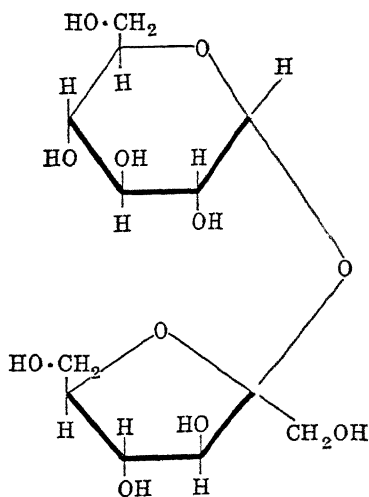


Fig. 27. Diagrammatic representation of Sucrose (Haworth).

chains of continuing units in cellulose. "And so, as Milton puts it:

'with many a winding bout  
Of linked sweetness long drawn out,'

we picture the sinuous track of glucose units in the continuous chain of the starch molecule." (Haworth.)

*Size of the Cellulose Molecule.* Chemical methods indicate that the average length of the cellulose chain is about 200 glucose units, a figure much below that given by ultracentrifugal sedimen-

tation, or by the Staudinger viscosity procedure.\* These physical methods, however, are concerned with the physical molecule or molecular aggregate arising from end-to-end as well as side-to-side aggregation of the simpler chemical units, a phenomenon directly observable in the "retrogradation" of starch (see further on). Hydrocellulose and oxycellulose represent disaggregations of the physical unit, favoring and often accompanying the chemical changes involved in the preparation of cellulose derivatives (nitration, acetylation, etc.).

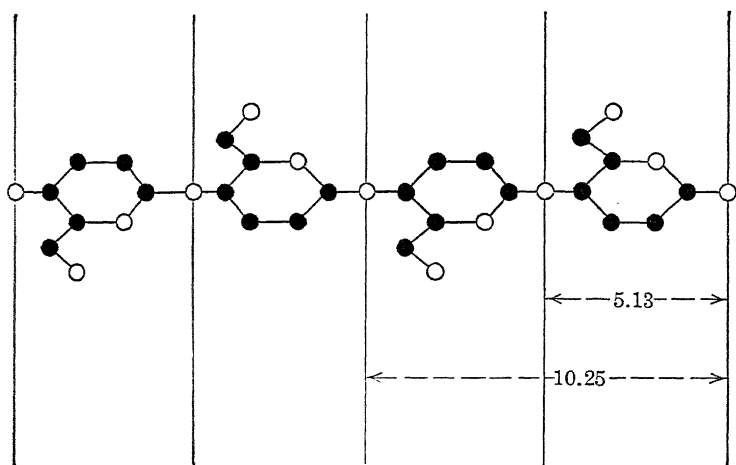


Fig. 28. Cellulose chain, based on X-ray data (Haworth) (dimensions in Angstrom units).

Dr. Wanda Farr (U. S. Dept. of Agriculture) and her collaborators at Boyce Thompson Institute for Plant Research (see

\* H. Staudinger, *Berichte*, 1926, 59, 3018; H. Staudinger and W. Heuer, *ibid.* 1930, 63, 222; H. Staudinger and R. Nodzu, *ibid.* 1930, 63, 721. See also paper by J. W. McBain and D. A. Scott, *Ind. Eng. Chem.*, 1936, 28, 470-3, who criticize Staudinger's earlier work, and point out that in a recent paper (*Chem.-Ztg.*, 1935, 59, No. 72,733, and No. 74,756) "Staudinger postulates a swarm theory of association to account for the properties of heteropolar colloids, such as his polyacrylic acids." The tendency toward molecular association is so strong in water solutions of simple straight-chain sulphonic acids, that in all but extremely dilute solutions "these simple molecules organize themselves into regular colloidal particles or micelles. The most striking point is that the simple ions do the same thing, forming the ionic micelle. This is extremely important because it shows that the forces of association are so great that they completely overcome the powerful electrostatic repulsions between these like ions and wholly submerge the influences which are discussed in the Debye-Hückel theory of electrolytes."

Contributions of the Institute, 1931-4) have followed microscopically the development of cotton fibers so as to seek out the smaller sub-units. W. K. Farr and S. H. Eckerson (1934, 6, 189-203, 309-13), by treating mature cellulose fibers for periods ranging from one-half hour to five days with strong HCl (sp. gr. 1.19) to remove non-cellulose constituents (which tests showed to be of a pectic nature), were able to isolate ellipsoidal particles of cellulose approximately  $1.5 \times 1.1 \mu$ , having their long axis parallel to the main axis of the cotton fibrils and a thin coating of pectic substance upon their surfaces, somewhat like capsulated bacteria. These ovoid structural units are, of course, very much larger than the primary molecular aggregates referred to by Haworth, but they are evidently one of the many successive serial groupings of matter whereby our present "ultimate" particles of matter build up into tangible units. They gave a typical Debye-Scherrer cellulose pattern on X-ray examination, and when treated with 18 per cent. NaOH gave the pattern of mercerized cellulose. W. K. Farr and W. A. Sisson (1934, Vol. 6, 315-21) conclude:

"Certain X-ray diffraction phenomena which heretofore have seemed to necessitate the assumption of the existence of hypothetical submicroscopic micellae are explained equally well by these microscopically visible particles of cellulose, observable as units in the young cotton fibers but united in the later stages of growth by non-cellulose cementing substances to form fibrils in which the cellulose particles can no longer be seen as individuals."

There is no reason why both submicroscopic and microscopic aggregations cannot co-exist, just as do sub-atomic units, atoms and molecules. Where mixtures of substances are in question, adsorbed layers of one constituent may serve as a "protector," or *if the layers cohere*, may stick the units together. In a paper read before the American Chemical Society, April, 1935, J. Alexander termed these latter substances *cohesive colloids* (see experimental data on starch, p. 322).

Along similar lines is the work of W. T. Astbury, R. D. Preston and A. G. Norman (Nature, 1935, 136, 391) on the X-ray examination of the effect of removing non-cellulosic constituents from vegetable fibers. The xylan\* (a polysaccharide,

\* Present evidence is that xylan consists of a chain of about 10 xylopyranose residues, terminated at one end by an arabo-furanose unit. (W. N. Haworth, E. L. Hirst and E. Oliver, J. Chem. Soc., 1934, 1917-23).

initially 19.8 per cent.) was progressively removed from the cellulosic fibers of manila hemp; but the X-ray photographs simply became more and more like those of fibers of low xylan content. The authors state that this favors the view "that the incorporation of xylan is a sort of mixed crystallization." Since slow growth in the cell would give ample time and opportunity for the accumulation of adsorbed layers of what would serve, under the conditions there, as a "cohesive colloid," this latter view seems preferable.

*The Chemical and Physical Structures in Starches.* It has long been recognized that starches may be separated into two portions (1) a water-insoluble fraction, formerly called "granulose," which gives a purplish color with iodine; (2) a water-soluble fraction, formerly called "starch cellulose," which gives a blue color with iodine. Later on the terms *amylopectin* and *amylose* came into use (Maquenne and Roux, *Compt. rend.*, 1903, 137, 88) for the insoluble and soluble fractions respectively, while others have used the terms  $\alpha$ -amylose and  $\beta$ -amylose, suggested by A. Meyer, *Ber. Deut. bot. Ges.*, 1886, 4, 337). Haworth prefers to use the terms amylopectin and amylose, pointing out that the terms  $\alpha$ - and  $\beta$ -amylose have no essential connection with any stereochemical difference in the basic starch units, as is the case in the now generally accepted new nomenclature for the carbohydrates and sugars.

The fact that methylated starches derived from potato, maize (corn), and waxy maize (which last gives a red-violet coloration with iodine) when examined by a gravimetric assay of the end group, all indicate a molecular weight for starch of about 5,000, or 25 glucose residues, and the further fact that the same results are given by the more highly aggregated amylopectin fraction as well as by the amylose fraction, favor the view that "the chemical unit of starch is of limited size, having an average molecular weight of about 5,000 and that these units undergo aggregations to physical units of much larger dimensions." "Amylopectin is, on this reasoning, considered to be a more highly aggregated state of starch than is amylose. Preparations of the latter revert to the highly aggregated condition of the former. It is understood that micellar aggregates of starches can be represented as bundles or assemblages of the chemical unit attached laterally by light valency forces, and the comple-

mentary hypothesis must also be advanced that the molecular unit of starch is capable also of longitudinal extension through the attachment of molecules end to end by processes of co-ordination. In either case the type of valency forces concerned must differ from those recognized in the principal valencies which unite the continuing units of  $C_6$  with one another in a chain-like manner to form the chemical molecule." (D. K. Baird, W. N. Haworth, and E. L. Hirst, J. Chem. Soc., 1935, 1201-5). These forces of aggregation probably are responsible for the fact that when examined by viscosity methods (*e.g.*, that of Staudinger) methylated and acetylated starches give indications of possessing a molecular weight about 3 or 4 times that found by chemical methods.

Haworth and his collaborators have also studied a graded series of break-down products of starch (dextrins) by chemical as well as by physical methods. The dextrins corresponding to an average of 5 to 12 glucose residues per molecule, show no tendency to undergo molecular aggregation to substances of higher molecular weight. On the other hand,  $\alpha$ -amylodextrin obtained by the action of barley diastase on amylose and representing "an arrested stage in the scission of starch to maltose or glucose," exhibited a remarkable capacity towards molecular aggregation. In this respect it resembled its parent amylose, but differed markedly from specimens of glycogen ("animal starch"), which displayed little or no tendency towards molecular aggregation.

The question as to the function of the small percentages of silica and of phosphorus found in most starches is still unsettled. Prof. T. C. Taylor (Columbia University) and his collaborators (J. Am. Chem. Soc., 1926-33) separated specially prepared and redissolved starch into two fractions by means of electrodialysis. The portion that migrated to the anode was considered to be  $\alpha$ -amylose (amylopectin), while the non-migrating fraction was classed as  $\beta$ -amylose (amylose). The amylose fractions in the main starches were found by Taylor to be as follows: (per cent.) potato, 97; corn, 85; tapioca or cassava, 83.5; rice, 82; wheat, 76.5. Taylor believes that the phosphorus is bound in the amylopectin fraction as a substituted phosphoric acid, and that the fatty acids (*e.g.*, oleic, linoleic, and palmitic), identified in corn starch, are similarly bound. Prof. Jesse E. Day (Ind. Eng.

Chem., 1936, 28, 237) found that it was practically impossible to remove the phosphates and silicates from sucrose and lactose which he used to prepare pure carbon.

Baird, Haworth and Hirst (*loc. cit.*) state that the stoichiometric relations of the phosphorus are obscure, since starches whose phosphorus content varies from 0.2 down to 0.01 per cent. can be made to yield products of very varied viscosities, so that "it is apparent that the latter property cannot be directly correlated with the phosphorus content." Haworth, Hirst and Waine (J. Chem. Soc., 1935, 1299-1303) say that the phosphorus appears to be chemically combined, but they "have not been able to trace any connection between phosphorus content and capacity to undergo aggregation." . . . "Our studies of starch and starch dextrans suggest the view that in native cellulose there may be molecular aggregation, and the fundamental chemical molecule is probably much greater than 200 glucose units in length. The reagents employed in preparing derivatives from native cellulose doubtless effect considerable disaggregation, a process which must be distinguished from that of a chemical break-down of the molecule."

### *Starch Considered as a Mixture of Substances*

Despite demonstrated differences in chemical constitution and in practical working properties, starches of diverse origins nevertheless exhibit such marked similarities that they are all classed as "starch." Whether amylopectin is simply a more aggregated form of amylose as Haworth's work indicates, or is chemically different from amylose as many earlier workers have believed, some understanding of the supermolecular structure of starches may be had by considering them as a mixture of substances, a view which brings to light the protective and the cohesive relationships of the several constituents. As Prof. M. Samec recently pointed out (Trans. Faraday Soc., 1935, 31, 395-410) the constituents of starch will vary with the methods used to separate them.

There are here epitomized some ultramicroscopic and other observations of J. Alexander (see J. Soc. Chem. Ind., 1936, 55, 206-9 \*), who used strong formic acid (about 90%) as a starch

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\* This paper was read before a Joint Symposium on Starch by the Divisions of Agricultural and Food Chemistry and of Colloid Chemistry of the American Chemical Society, on April 25, 1935.

solvent. Care must be exercised, as the acid is highly corrosive and can make bad "burns." In it the starch granules quickly swell and burst, so that vigorous initial stirring is essential to avoid the formation of "lumps." On standing overnight the dispersions become more fluid and uniform on stirring, without degeneration to glucose, though this may occur on long standing.

Formic acid dispersions containing 10% of corn, potato, tapioca, wheat, and rice starches all showed a marked Faraday-Tyndall effect, and though fairly clear became noticeably clearer on stirring. This *thixotropic optical effect* was least marked in corn starch.

Ultramicroscopic observations were made with the Leitz dark field, at several magnifications. The ultramicroscopic fields showed an undifferentiated background containing relatively few, non-motile ultramicros. But when water was worked under the cover-glass into the field so that the formic acid was materially diluted, an immense number of ultramicros immediately appeared, some actively moving, others aggregated into branching fibers and alveolar cell-like structures. Though the appearance of the fields varied in different experiments and even in different areas of the same experiment (largely because of variation in the speed and the degree of dilution of the solvent acid), in general the newly appearing ultramicro groups and fibers appeared to be entrapped within a clear matrix or sheath. In some areas there were seen fibers of clearish material, with adherent or entrapped ultramicros. In a few areas (corn, tapioca) there appeared structures resembling miniature starch grains, although the viscous dispersions had been well stirred and showed no sign of such structures prior to dilution.

On diluting the formic acid/starch dispersions with about four times their volume of water, coagulae of varying size and nature separated from the turbid fluids. With wheat and rice starches the coagulae were flocculent and non-adherent to the stirring rod; with potato and tapioca starches the coagulae were rubbery and clung to the rod. Corn starch was intermediate. Neither the turbid dilution fluid nor the coagulum of tapioca starch showed the presence of reducing sugars when tested with Benedict's solution, nor a blue coloration with iodine; but on addition of some boiled potato starch paste to the mixture of



turbid fluid and iodine, a typical "starch blue" at once appeared. The coagulum gave a red-brown coloration with iodine; but with strong  $\left(\frac{n}{10}\right)$  iodine solution some blue areas were seen on microscopic examination.

A ball of "amylopectin" precipitate, prepared as above from potato starch and washed for one hour in running tap water, showed on colorimetric test a pH of about 4. On standing 36 hours it became viscid and clear, and on stirring with cold water gave a viscous solution which showed no reduction when boiled with Benedict's solution, but did give a typical "starch blue" with iodine. A fragment of the original coagulum which had remained for 48 hours in contact with much water, was white and undispersed though still quite acid; with iodine it gave a yellow-brown coloration, and ultramicroscopically it appeared as a mass of aggregated ultramicros. The water in which it had soaked gave a brownish color with iodine and was full of small, actively moving ultramicros.

These results incline one to the view that in the course of coagulation the less soluble "amylopectin" fraction has entrapped part of the "amylose," just as fat globules are entrapped by the coagulating casein in whole milk. This gives the coagulum a certain degree of dispersibility even when dried, and accounts for the fact that on repeated re-solution and re-precipitation of the "amylopectin" fraction, the precipitate progressively diminishes in dispersibility in cold water. The insolubility of starch granules in cold water would seem to be due to the fact that its exterior surfaces are mainly insoluble amylopectin; while the dispersibility of dried boiled starch paste would indicate that there the more dispersible and protective amylose constitutes mainly the exterior phase. Further support for this view lies in the fact that when starch granules are triturated with clean sand, or ground dry in a pebble mill, they become largely dispersible in cold water (C. L. Alsberg and E. P. Griffing, *Proc. Exp. Biol. and Med.*, 1924, 22, 60; 1925, 23, 142-3. The latter paper records analogous effects on the dry grinding of gelatin and of gluten and its constituents, gliadin and glutinin. See also the effects of grinding on karaya gum, etc., J. Alexander, *J. Am. Chem. Soc.*, 1921, 43, 434-40).

*Colloidal Protection as a Factor in the Behavior of Starches*

Practical experience with commercial starches and their various conversion products (soluble starches, white and yellow dextrines, British gums, etc.) indicates that there exist within this broad group constituents which may be considered as belonging to two classes: (1) those which tend to remain in dispersion; (2) those which tend to aggregate more or less rapidly, depending on specific nature, concentration, temperature and time. The behavior of a product, or of a mixture of products, depends largely on the nature and relative proportions of its aggregating and its dispersible or protective fractions.

Thomas Graham (Phil. Trans. Roy. Soc., 1861, 151, 183-224) was perhaps the first to call attention to protective colloid effects, and, as it happens, with a carbohydrate, caramel (see p. 151). Zsigmondy ("Colloids and the Ultramicroscope," 1909, p. 43) in commenting on the protection against coagulation offered by "the sugar and intermediate brown substances" (so Graham termed them) emphasizes the fact that substances capable of diffusion are able to exert a protective effect. Working with a sample of soluble starch given him by Prof. Lintner, Zsigmondy found that a 3% solution, prepared at the boiling point, gave a light-cone which was not resolvable ultramicroscopically. On standing for a few days in a cold room, the clear solution became opalescent, then in three or four weeks milky white. Ultramicroscopic examination now revealed the presence of ultramicros about 50-100 m $\mu$  in size.

Zsigmondy states that the development of ultramicros in the starch solution vividly recalls the formation of gold particles in ruby glass (see p. 258), or the process of the formation of colloidal selenium. Whereas with these elements (Au, S, Se) particle growth is speedy at the proper temperature, "partially because of the smallness of the crystalloid molecule, its very much more complete diffusion, and probably because of a great specific rapidity of growth, that of the starch particles takes place with extreme slowness. *It may also be assumed that the starch solution itself contains constituents which oppose growth.* (Italics mine.) With soluble starch, reversion to the original molecular state of subdivision takes place at about 100° C., and with ruby glass at white heat."

On cautiously adding some 50% gum arabic solution to a 10% dispersion of potato starch in cold 90% formic acid, the protective gum could be mixed with the starch with but a slight reversible local precipitation. On continuing to add the gum solution, the beneficial effects of double colloidal protection (see p. 155) were had, and the "amylopectin" fraction came out mainly in colloidal dispersion. The colloidal protective action of starch through its effects on crystallization forms were observed where the formic acid dispersions were neutralized with ammonia (giving ammonium formate), and also where potassium iodide segregated on slides tested with iodine solution (see J. Alexander, *loc. cit.*).

The surprising effects arising from the interplay of crystallization forces and specific protective colloids, leads one to suspect that the size, shape, and nature of many biological structures may be thus largely dominated (see p. 357; also J. Alexander, *Science*, 1922, 56, 323-6). Plant and animal cells and circulating fluids abound in substances capable of acting as protectors, so that a precipitate forming from such protected reacting fluids would tend to be highly colloidal because of double or plural protection, (*e.g.*, as in milk, Lippmann's "grainless" emulsion, etc.). Where an elongated molecule of molecular group is formed catalytically, or grows out from a specific area, somewhat as ice crystals sometimes do from freezing gelatin, adsorption of a colloid layer at the long sides would tend to limit or to prevent sidewise growth. *If, however, these adsorbed colloid layers tend to cohere*, we would have what might be justly termed a *cohesive colloid*, a variant of the separating action of protective colloids, which usually effect dispersion. The thin, non-birefringent pectinous layer\* observed by Dr. W. K. Farr as a coating to the tiny cellulose units she isolated (see p. 314), seems to represent a cohesive colloid that serves as an effective cementing material in the construction of cellulose fibers from the smaller units.

Change in the protective capacity of a protector is generally followed by change in the degree of aggregation of the protected system or by change in its degree of dispersibility. Thus on adding ferric chloride to a gum arabic/oil emulsion, the protective

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\* Cellulose is unaffected but this layer is stained by ammoniated ruthenium oxychloride ( $\text{Ru}_2(\text{OH})_2\text{Cl}_4 \cdot 7 \text{NH}_3 \cdot 3 \text{H}_2\text{O}$ ), known as *ruthenium red*, and used as a microscopic stain for pectin, plant mucin and gum.

gum is coagulated and the oil separates out. In the case of starches, small quantities of specific catalysts or enzymes may wield such decisive influence on degree of dispersion. In 1908 J. Wolf and A. Fernbach (Compt. rend. 1908, 137, 129) obtained from green cereals an enzyme, *coagulase*, having the power of *precipitating* starch from its solutions. Its action was inhibited by the serum of rabbits immunized with it (C. Oppenheimer, "Fermente," 4th ed., 1913, p. 282). To this enzyme they attributed a material function in the separation of starch in the cell. Apart from the well-known amylases which can disperse starches, there are evidently then other enzymes capable of directing their aggregation. It is also possible that the synthesis of increasing quantities of *cohesive colloids*, which later aggregate, may result in the adsorptive removal of a sol of amylose.

## CHAPTER XVIII

### BIOLOGY AND MEDICINE

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- 2—Functional Life—Living vs. Dead
- 3—Active and Latent Functional Life
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- 5—Enzymes
- 6—Cytology
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- 9—Genetics
- 10—Some Factors Influencing Development
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- 12—Physico-chemical Determinism in Life and Disease
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32—Nervous System: Psychiatry: Consciousness and Mentality

## BIOLOGY AND MEDICINE

*Biology*, centering in the study of living units, their structure, activities and classification, is divided into many subsidiary sciences, *e.g.*, taxonomy (classification), cytology (study of cell structure and function), genetics (study of inheritance), physiology, biochemistry, etc. Therefore biology has many correlations to physics, to chemistry, and to physical chemistry—including colloid chemistry.

*Medicine* involves many sections of biology and their application to understanding the various bases of health and disease, with the objective that health may be maintained, and disease cured or its consequences ameliorated. In addition to purely biological aspects (anatomy, bacteriology, physiology, biochemistry, etc.), psychological and sociological aspects are also of great importance in medicine; for many if not most human ills have a psychological concomitant or cause, and may be greatly helped by proper psychological approach. The practising physician deals with human hearts and mental states, as well as with structurally or physiologically defective specimens of genus *Homo*.

*Structural Life—Living vs. Non-life Entities.* In attempting to draw the line of cleavage between living and non-living entities, a task which is by no means simple, we must define what we mean by "living" entities or units. In its broadest sense a living unit or entity is one which can direct chemical changes catalytically, and at the same time reproduce. Genes (p. 342) and ultrafilterable viruses (p. 329) are among the simplest known life units. In smallness they approach molecular dimensions, and may be considered as *autocatalytic catalysts*, that is, catalyst particles which can catalyze the formation of their duplicates from simpler chemical substances. Apparently, all living units have the additional power of undergoing more or less rare sharp deviations from the standard structure and function, through "mutation" which leads to the evolutionary development of new types; but self-reproduction is the most basic criterion as to whether a unit belongs to the category of life, as distinguished from non-life. The essen-

tial fact distinguishing true life units is their ability to increase the number of their kind by direction of chemical changes whereby non-living and generally simpler molecules and masses are built into the catalytic and reproductive structure of the living entities.

In contrast to living entities, *non-life* entities are those whose increase in numbers is not through the direct catalytic action of a pre-existing or parental unit of that type. For example, molecules of sulphuric acid are typical non-living entities.

### FUNCTIONAL LIFE—LIVING VS. DEAD

In a more restricted sense of the term "living," we may call "living" any cell, tissue or organ from a living unit while it carries on the processes it ordinarily did during the functional life of that unit.\* Thus a frog's heart may be kept "alive" and beating after removal, though the frog is functionally dead. Dr. Alexis Carrel (Nobel Laureate, Rockefeller Inst. for Medical Research) by proper precautions and continual renewal of the embryonic juice culture medium, has kept a fragment of chicken heart muscle tissue alive and growing for over a quarter of a century. This brings out the fact that where large numbers of cells are associated in a community life, as with multicellular plants and animals, most cells become so differentiated or specialized (as in organs) that they can no longer carry on an independent existence. Consequently, if one organ or even a small group of cells is attacked, the whole organism may fail. Thus the deadly prussic or hydrocyanic acid (HCN) and the *almost equally poisonous* hydrogen sulphide ( $H_2S$ ) produce functional death by inactivating certain cells in the medulla which control the heart and respiration.

The notion that functionally living things must "breathe" and "move" is a purely anthropomorphic one. With hibernating animals (hedgehogs, woodchucks, bears) visible breathing ceases for long periods, the heart (its irritability is increased) beats just enough to maintain a sluggish circulation, and the body tem-

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\* See also p. 246 on the difference between somatic and cellular death. In this more restricted sense, sterile and castrated animals are said to be alive, as are isolated members of one of the sexes—for example, the sole surviving heath-hen that died recently on Martha's Vineyard. But when we analyze down to the ultimate units of life, we see that self-reproduction is the essential without which the species would sooner or later disappear.

perature falls nearly to that of the surroundings. The demand for oxygen is reduced to a minimum which may be partially met by diffusion. The animal lives at a reduced rate, consuming its accumulated reserves. Fakirs and magicians (*e.g.*, Houdini) are able to endure temporary burial by a rigid control of body processes; any sudden panic, leading to a struggle to escape would no doubt be quickly fatal. The condition produced by successful practitioners of this feat is a partially suspended animation, analogous in some respects to an artificial hibernation.

### ACTIVE AND LATENT FUNCTIONAL LIFE

In still another sense a unit is said to be alive if it retains the power to resume active life processes (catalysis and reproduction) when suitable conditions are re-established. Quite a large number of plants and animals are able to revive after prolonged desiccation accompanied by a more or less complete cessation of active life—*e.g.*, many protozoa, bacterial spores, the lung fish. In the Antarctic, Byrd reports finding primitive plants whose activities re-begin whenever conditions permit during the long "summer." This resting or latent form of life will persist so long as the basic biocatalysts and their essential modifiers and supporting structures do not suffer changes beyond certain limits. The vitality of "germs" (microorganisms, spores, bacteria, etc.) and even of seeds is amazing. While high temperatures are fatal to all life processes, many organisms stand extremely low temperatures for indefinite periods (*i.e.*, immersion in liquid air). Prof. Charles B. Lipman (University of California), using rigorous precautions against contamination, found viable bacteria in coal taken 1800 feet below the surface, and also within adobe bricks from old Spanish Missions, and from Aztec and pre-Inca ruins. He believes that the peat-like material which became coal millions of years ago, was extremely rich in bacteria, and that some of their spores still survive. (*J. of Bacteriology*, 1931, 22, 183-198; "Science," 1934, 79, 230.) He has also isolated an autotrophic bacterium from petroleum derived from a well 8,700 feet deep ("Science" 1932, 75, 192). An alga (*Phormidium*) grows in Beryl Spring (Yellowstone Park) at a temperature of 89° C. (R. B. Harvey, *Science*, 1924, 60, 481).



In 1879 Dr. W. J. Beale (Michigan Agricultural College) buried seeds of 20 different kinds of plants, samples being taken up every five years for test. After 40 years' burial, half of the species produced sprouts. (Am. J. Botany, 1922, 9, 266-269). Dr. J. W. T. Duvel (U. S. Dept. Agriculture) in 1902 buried seeds of 107 species, and found that after 10 years 69 species grew, while after 20 years burial 51 species grew. Seeds of wild plants and weeds were most hardy, whereas cereal and legume seeds, and cultivated plants generally, readily died out, and seem to depend upon human agencies for their perpetuation. (J. Agricul. Sci., 1924, 29, 349.)

It is known that "dormant" lettuce seed will germinate when exposed to white light, as well as to yellow, orange and red; but violet, blue and green light fail to stimulate to germination. (See Smithsonian Pub. No. 3334, 1935, by L. H. Flint and E. D. McAlister.) This suggests light as a factor in the seasonal sprouting of seeds.

Bequerel (Compt. rend., 1906, 26, 1549) reported on the germination of 550 species of seeds (representing 30 important families of plants), which had been stored from 25 to 135 years at the Jardin des Plantes, Paris. The oldest that germinated were 80 years old. Wheat has been shown to survive as long as 19 years, but much more hardy is the myth about "mummy wheat" which probably had its origin in the deposit of seeds of recent crop by native guides, anxious to please explorers of Egyptian tombs.

In 1930 most unusual rains in Death Valley, California, were soon followed by a luxuriant growth of flowers in the erstwhile desert, arising from seeds carried there by winds and long dormant. (See N. Y. Times, June 6th, 1930.) Similarly, in Palestine, the spring rains bring a gorgeous but fleeting floral display on the otherwise rather bare hills.

The spores of anthrax are so extremely resistant that whole fields have become infectious because of the burial in them of sheep dead of this disease, which is probably the "murrain" mentioned in the Bible. It is also known as "wool-sorters' disease" because it was often carried to human beings in the wool and hair of animals, *e.g.*, in shaving brushes. Sterilization of commercial products of this kind is now compulsory, and animals dead of anthrax must be cremated or else buried very deep.

## MICROORGANISMS

*Bacteria.* Bacterial suspensions exhibit many of the phenomena shown by other colloidal or near-colloidal dispersions, *e.g.*, kinetic Brownian motion which is inhibited by electrolytes. The motion may in part be due to the unbalanced liberation of gases or other diffusible products. Bacteria may also be flocculated and precipitated by electrolytes. The smaller, approximately spherical bacteria average about  $1\mu$  in diameter, which means that they have about 60,000 sq.cm. of free surface per gram of mass, and much of the mass may be water. It is estimated that a yeast cell  $5\mu$  in diameter contains only 0.000,000,-009,817 mg. of "solid" matter.

Bacteria have a highly developed surface specificity and a much more complicated and changing internal structure than is disclosed by microscopic examination. Thus as the tubercle bacillus develops (Dr. Morton Kahn, Cornell University), it seems to pass from a stage in which the Ziehl-Neelson stain is *not* acid-fast to one in which the stain *is* acid-fast; and tiny granules which appear within the bacillus show the same transition (Eleanor G. Alexander, Proc. Soc. Exptl. Biol. Med., 1934, 31, 1102). Bacilli are agglutinated or flocculated by highly specific substances (agglutinins) which generally appear in the blood-serum of a person receiving the specific bacterial poison or antigen. In the Widal test for typhoid, lysis of the bacteria follows their agglutination.

Prof. E. K. Rideal (Cambridge University) attributes the adsorptive selectivity to the submicroscopic inhomogeneity of the bacterial surface. (Fifth Report on Colloids, Brit. Assn. Adv. Sci., 1923.) The mere fact that a bacterium may move this way or that in an electric field according to the nature of its *net* charge, must not close our eyes to its inherent complexity.

Besides suffering great internal and surface changes with variations in the milieu, the individual bacteria may swell or shrink and thus produce a great change in the viscosity of the bacterial suspension (see p. 146; also I. S. Falk, Alexander's Colloid Chemistry, Vol. II, pp. 543-55).

*Filterable Viruses and Mosaics.* With the discovery of bacteria as the cause of certain diseases, it was hoped that specific bacteria would be found in all infectious diseases. Quite a num-

ber of infectious diseases were, however, traced to protozoa (*e.g.*, amebic dysentery, malaria, African sleeping sickness), but in many other cases no infective organism was found. Pasteur, unable to find the causative agent (virus) for rabies, expressed the view that there were such agents invisible to the microscope. Iwanowski (1899) in studying the mosaic disease of tobacco (so called because it produces a peculiar mottled leaf) found that the juice of diseased plants would infect healthy plants, even after filtration through dense porcelain filters which would prevent the passage of ordinary bacteria. Beijerinck who had independently made the same discovery in 1897, showed that the infection could be thus carried through whole series of plants, indicating that the filterable principle is living. In nature there are insect carriers of the virus.

A search for these ultramicroscopic "filterable viruses" at once began, and among those which have been identified with specific diseases are the following:

*Plants.* Mosaics of tobacco, of tomato, of the Jamestown or Jimson weed, and of cucurbits (squash, cucumbers, etc.), generally carried by insects.

*Insects.* Jaundice of silkworms; sacbrood of bees; the wilt disease of the gypsy moth caterpillar.

*Birds.* Chicken plague; epithelioma contagiosum; leukemia and certain malignant tumors of chickens; an epidemic disease of blackbirds.

*Mammals.* Cow-, sheep- and goat-pox; pleuro-pneumonia of cattle; rinderpest; rabies; hog cholera; swamp fever of horses and South African Pferdesterbe; catarrhal fever, heart water, and Nairobi disease of sheep; agalaktia contagiosa in goats; foot and mouth disease.

*Man.* Smallpox; warts; mumps; dengue (break-bone fever); measles; molluscum contagiosum; pappataci fever; herpes; trachoma; anterior poliomyelitis (infantile paralysis); meningitis; and probably epidemic encephalitis, chicken-pox and common colds.

Many bacteria develop from tiny spores, and these or some intermediate form of the organism may be small enough to pass a filter usually impervious to fully developed bacteria. Besides, as has been pointed out on page 127, distortable bodies may be readily forced through interstices in filters which will hold back much smaller non-distortable particles. A. Krogh states that

red blood corpuscles pass through filter paper whose pores retain quantitatively precipitates with much smaller particles: "The pressure available for such a passage cannot exceed the height of the fluid in the funnel." The presence of colloidal protectors may also be a factor here, as also pointed out on p. 126, for they, too, may assist particles to pass through pores in filters and membranes.

W. M. Stanley ("Science," 1935, 81, 644) isolated from the juice of infested tobacco plants a crystalline protein possessing the properties of tobacco-mosaic virus. One cubic centimeter of a 1 to 1,000,000,000 dilution of the crystals usually produced the mosaic disease, and solutions of the crystals, when injected into animals, gave a specific precipitin, indicative of chemical individuality. The fact that this protein forms colloidal dispersions and probably exists in colloidal form when active in the tobacco plant, becomes evident from Stanley's description of the properties of the product and its mode of preparation.

Though insoluble in water, the protein dissolves in dilute acid, alkali or salt solutions. Its 0.1 to 2 per cent. solutions are opalescent (Faraday-Tyndall effect), fairly clear between pH 6 and 11 and between pH 1 and 4, dense whitish in appearance between pH 4 and 6. The protein is "denatured" and its activity lost by heating to 94° C. when it coagulates; also at high alkalinity (about pH 11.8) or high acidity (pH less than about pH 1). In preparing the crystals, a globulin fraction was salted out by ammonium sulphate and remaining color removed by a little lead subacetate at pH 8.7. The active protein was separated from an inactive protein fraction by adsorption on celite\* at pH 4.5 and elution at pH 8. Crystallization was accomplished by salting out slightly acid dispersions of the active protein; but dialysis gave only amorphous material.

It should be remembered that mixtures may form perfectly defined crystals (*e.g.*, alums, many minerals). But whether this tobacco-mosaic virus protein is one substance or a mixture, Stanley regards it "as an autocatalytic protein which, for the

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\* *Celite* is a purified diatomaceous earth (silica) having a greatly extended surface. *Elution* is a term coined by Willstätter to describe desorption of an adsorbed substance. For details as to Willstätter's development of this procedure to concentrate enzymes, see his paper in Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied," 1928. Dr. Stanley is at Rockefeller Inst. for Medical Research, Princeton, N. J.

present, may be assumed to require the presence of living cells for multiplication." Every form of living thing, however, demands suitable surroundings, conditions and food for life and self-duplication, and biology tells us of many queer conditions demanded by adapted organisms, some of which require a succession of living hosts. The fungus "rust" of wheat must spend part of its life in certain barberries. Consider the devious life cycles of many worms, *e.g.*, the hook-worm and the tape-worm. Following floods of the Mississippi, the Bureau of Fisheries returns to the river many fish collected from the temporary lakes or ponds, mainly to help the fresh-water pearl industry. For in its early, free swimming stage, the pearl mussel must live for a time in the gills of certain fish which act as "nurse maids" for it.

If, as seems likely, this mosaic virus-protein can catalyze and direct chemical changes and at the same time duplicate itself, it is an autocatalytic *catalyst* and must be regarded as *living*. It thus closely approximates the hypothetical *moleculobiont* postulated by Alexander and Bridges (See their paper on "Some Physico-Chemical Aspects of Life, Mutation and Evolution," Vol. II of Alexander's Colloid Chemistry. See also pp. 369, 391.)

*Bacteriophage.* In 1915 F. W. Twort (Lancet, 1915, 2, 1241) while investigating the nature of ultramicroscopic or "filterable" viruses, observed a strange progressive dissolution of bacterial colonies. Since the lytic effect could be transferred from colony to colony in series, Twort regarded it as a transmissible disease of bacteria, caused by a filterable virus. Subsequently, F. d'Herelle (Compt. rend., 1917, 165, 373) found that *one drop* of an ultrafiltrate from a very dilute bouillon emulsion (pH 7.2 — 7.8) of the evacuation of a patient recovering from dysentery caused by the Shiga bacillus, would within four or five hours render perfectly limpid 10 cc. of a turbid young culture of these bacilli containing 300 to 400 million bacilli per cc. If this limpid fluid be filtered through a porcelain filter candle, one drop of it exhibits the same "bacteria-eating" or bacteriophage power as the original, and the phenomenon may be carried out in a continued series, becoming stronger rather than weaker, until, after a few passages from culture to culture, a billionth of one cc. of the filtrate will "dissolve" all the bacteria in 10 cc. of a Shiga bacillus culture.

d'Herelle regards bacteriophage as "a living colloidal micell," a view largely accepted; but some consider it as a kind of enzyme liberated upon the disintegration of bacteria. Bacteriophages are as a rule highly specific, although the "phage" of the Shiga bacillus will also attack the Flexner dysentery bacillus. Success has been reported in treating diseases (*e.g.*, furuncles and carbuncles due to staphalococcus infection) with bacteriophage, and d'Herelle believes that the water of the sacred, but sewage-contaminated Ganges River at Delhi, in which so many bathe and of which so many drink, may offer them a curative or preventative in the form of a bacteriophage along with infective bacteria. It is not to be recommended, however, that safety from infection be sought in super-contamination.

Prof. J. J. Bronfenbrenner (Washington University) took moving picture films with Dr. H. Roger at Rockefeller Institute for Medical Research, showing a bacterial emulsion which had been inoculated with bacteriophage. A certain bacterium in focus attacked by the "phage," apparently swelled and burst or "exploded" so rapidly that it was difficult to follow its dissolution from frame to frame of the film.

Some notion of the size of virus and bacteriophage particles may be had from the following table of Prof. H. Bechhold (Frankfurt University) taken from his paper in *Kolloid Zeitschrift*, 1934, 67, 76, which gives his results as determined by filtration and by ultracentrifugal methods.

TABLE XXVI  
SIZE OF ULTRABIONTS

	Method of Determination		
	Ultra-centrifuge	Filtration	% diff.
Smallpox.....	200 $m\mu$	125—175 $m\mu$	—25
Herpes.....	200	100—150	—38
Canary-virus.....	120	125—175	+25
Infect. Ectromelia* (Mice).....		100—150	.....
Chicken-pest.....	110	60—90	—30
Bacteriophage (WL).....	90	.....	.....
C16.....	90	50—75	—30
C21.....	75	30—45	—55
L.....	75	30—45	—55
Mosaic Virus.....	50	.....	.....
Bacteriophage D20.....	50	20—30	—50
Foot and Mouth Disease.....	.....	8—12	.....
Bacteriophage S 13.....	20	8—12	—55

\* Congenital absence of limbs.

## ENZYMES \*

The changes which occur in most biological processes are remarkable, not only because of their profound nature, but also because they are produced rapidly, at comparatively low temperatures and in the presence of dilute reagents. With apparent ease the living organism disintegrates proteins, oxidizes carbohydrates and fats and synthesizes substances of great complexity. High temperatures and powerful reagents which would be destructive of life are necessary to bring about changes of this character under ordinary laboratory conditions.

The high efficiency of the biological juices was once thought to be due to a mysterious "vital force," but this idea was disproved in 1895 by Büchner, who isolated from yeast triturated with sand, a lifeless zymogen or enzyme which had the power of converting sugar into carbon dioxide and alcohol. Enzymes (pepsin, diastase, pancreatin, papain, lipase and the like) are colloidal catalyzers, whose existence seems to depend on the presence of adsorbed protectors; for the more they are purified the more unstable they become. They are coagulated and inactivated by shaking, heating, electrolytes and so on, all of which cause coagulation of colloidal solutions with a decrease in their free surface and in the activity of their particles. The effective acidity (pH) of the solution in which an enzyme happens to be largely influences its action, probably by regulating its degree of dispersion and electric charge, which in turn affect free surface, adsorbability and kinetic activity.

The soluble and insoluble forms of enzymes are termed *lyo-* and *desmoenzymes* respectively (Willstätter).

Hair and skin color seem to depend upon the activity of oxidizing catalysts (usually enzymes) within certain cells, which determine the formation of colored melanins. Cells without such catalysts develop white hairs or "white" skin. This effect is shown, *e.g.*, in the Dalmatian dog, many of whose black spots develop after birth. In Haiti, a negro was treated by a voodoo doctor with some remedy that contained hydrocyanic (prussic) acid, obtained perhaps from cassava root. The dose nearly killed the patient; but, according to reports in the press, his skin

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\* See remarks on catalysis, p. 39; also a review entitled "Recent Advances in Enzyme Chemistry," by E. Waldschmütz-Leitz, in *Chemistry and Industry*, 1936, 55, 620-6. The term *enzyme* means *in yeast*.

gradually turned white. This report, if confirmed, is explicable on the view that the melanin-producing catalysts in the skin cells had been irreversibly damaged.

Enzymes are called into activity, in many cases, by the introduction of activators or the removal of inhibitors. Among the examples given by Waldschmidt-Leitz (*loc. cit.*) are the following: trypsin is activated by enterokinase from the intestinal wall, the two forming an easily dissociable compound; the lipase in castor beans (*Ricinus*) is activated by products (probably proteases) set free by the proteolytic seed enzymes, so that a definite successive order and equilibrium exists in the germinating seeds; malt contains an amylokinase which activates amylase. Balls and Swenson (J. Biol. Chem., 1934, 106, 409) found in egg proteins an inhibitor of the normally occurring trypsin; thinning of the egg proteins, which occurs on long storage, may be retarded by injection of the inhibitor and accelerated by injection of enterokinase.

Enzymes appear to act by forming with the substrate a compound of indefinite and unstable character, probably, as Sir W. M. Bayliss suggests ["The Nature of Enzyme Action"], a colloidal adsorption compound, which breaks down, liberating the enzyme again to continue the action. A. Croft Hill (J. Chem. Soc. 1898, 73, 634) showed that the action of enzymes may be reversible, but in the organism reversion is prevented by the diffusion, dilution, or peristaltic removal of the products formed. Where increases of concentration occur in cells, tissues or organs, synthetic processes may be induced by enzymes. *Concentration changes must follow variation in the permeability of membranes, e.g., cell-walls, tissues.*

Ultramicroscopically, enzymes show a multitude of colloidal particles in very rapid motion. Any substance immersed in such a solution, providing its electric charge or free fields of force permit the close approach or concentration of the enzyme at its surface by adsorptive action, must undergo a terrific bombardment, and it seems likely that enzymes produce their effects by virtue of their specific surface actions (which is influenced by the hydrogen ion concentrations of their solutions) and by the motion of their particles.



To see if this idea could be experimentally verified, J. Alexander followed ultramicroscopically the action of diastase on starch grains and the action of pepsin on coagulated egg albumen.

The diastase ultramicros, maintaining their active motion, gradually accumulated about the starch granules, which after a time showed a gnawed or ragged margin. The adsorption and motion of only the larger ultramicros could be followed, but the bright appearance of the field indicated that numerous smaller particles were present, and some of the intermediate size were seen. The albumen specimen was a dilute solution of egg white, heated nearly to boiling. It was opalescent, and showed a field full of bright, rapidly moving ultramicros which immediately clumped or coagulated into large, motionless masses upon the addition of a droplet of pepsin solution (Fairchild's containing 15 per cent. of alcohol by weight). Upon "activating" the pepsin with a droplet of decinormal hydrochloric acid, the large groups burst into small groups and isolated ultramicros, which at once resumed their active "dance." Soon, however, the albumen particles began to grow fainter and disappear, the field meanwhile becoming brighter and brighter, indicating that simultaneously smaller ultramicros or amicros were being formed. The addition of pepsin to a test tube of the opalescent albumen solution caused it to clear gradually at room temperature.

### CYTOLOGY \*

Physiological chemists have made illuminating researches into the chemistry of cell metabolism, and cytologists have mainly by microscopical methods accumulated a wealth of interesting albeit unexplained facts, the elucidation of which will lead us still nearer to an understanding of the mystery of life processes.

When a cell undergoes *mitosis* (or *karyokinesis* as it is also known), some of the constituents of the nucleus appear as a long irregularly twisted thread or *spireme* (loose skein), which then becomes more open but shorter (open skein). The open skein splits into short segments, frequently U-shaped; these split and divide equally on either side of an equatorial plane, and then move toward the two star-like polar centers (*amphiasters*),

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\* The reader should look up a paper entitled "The New Cytology" by Dr. Alexis Carrel (Rockefeller Inst. for Medical Research, Nobel Laureate) in Science, 1931, 73, 297-303.

where they fuse. By constriction at the equator the cell now separates into two parts, each of which develops further into a separate cell.

Since the substances comprising the skein segments are readily stained by the microscopist's dyes, they are called *chromatin* substances, and the structures are called *chromosomes*. Most heritable characteristics which have been studied are transmitted through the chromosomes, which vary both in number and character with different plants and animals.

The genetic evidence (see p. 342) is that the chromosomes consist of a long chain or string of ultramicroscopic colloidal units termed *genes*, surrounded by their catalytic products to which the group name *chromatin* is given. The gene-string must maintain its identity during mitosis, for it is incredible that the genes scatter and reassemble in the same precise order each time a cell divides. The following outline by Dr. C. B. Bridges (Carnegie Institution) of the chromosomal cycle in cell division, as it occurs in the marine worm *Ascaris megalocephala*, is from Alexander's Colloid Chemistry, Vol. II, p. 36. The standard reference book in cytology is "The Cell in Development and Inheritance," by Prof. Edmund B. Wilson (Columbia University):

Stage	Gross Chromosomal Picture
Interphase—	Gene-string denuded of chromatin, and is invisible.
Prophase—	Gene-string ready to split, appears in loose spirals which shorten after developing a pellicle.
Metaphase—	The double coils unravel into two coils within the pellicle. The coils acquire separate pellicles and move as a double unit to the equator of the cell.
Anaphase—	One-half of each doubled chromosome moves to the opposite poles of the cell along the astral rays of the polar bodies, which also become doubled in the metaphase stage. The cell splits.
Telophase—	The chromosomes meet near the polar bodies in the new daughter cells; the chromosome pellicles distend and fuse, reforming the nucleus. The gene-strings have become denuded of chromatin, and are again invisible. The cycle begins again.

Some rough notion of the size of cells as compared with molecules is given by the estimate of Hofmeister that a liver cell

contains more than 200,000 billion molecules, among them being 50 billion protein molecules (average atomic weight 16,000), 150 billion lipid molecules, and 2,000 billion crystalloidal molecules of low molecular weight.

The problem of investigating the colloid-chemical changes underlying the microscopical picture of mitosis and its accompanying chemical changes, is a most formidable one; but once it is closely envisaged, some vulnerable points will probably be found. A beginning has already been made by R. Chambers (N. Y. University), A. Heilbronn, L. V. Heilbrunn, W. Seifriz (Univ. of Penn.) and others. The micro-method of Freundlich and Seifriz (*Zeit. phys. Chem.*, 104, 233-61) (which consists in pulling a tiny [ $18 \mu \pm$ ] particle of nickel through a gel by an electro-magnet of known power) shows that the inner protoplasm of the unfertilized egg of an echinoderm (*Echinarachnius parma*) has about the viscosity of concentrated glycerin, while the peripheral layer has the consistency of a soft gelatin gel [Seifriz, *Brit. J. Expt. Biol.* 1924, 1, 431-42].

At mid-mitosis the cytoplasm about each amphiaser has the consistency of a still plastic gelatin jelly, while the peripheral protoplasm of the egg becomes as viscous as bread-dough. Following the completion of mitosis, the viscosity drops again in preparation for another division. L. V. Heilbrunn investigated the viscosity of cellular constituents by centrifugal methods [1920 *J. Expt. Zool.* 30, 211-37].

If in the middle of mitosis (*metaphase*) the egg be subjected to slight pressure, the whole karyokinetic spindle-shaped structure collapses, resembling in this respect (as Seifriz points out) the gel of iron oxide described by Schalek and Szegvary [*Kolloid-Z.* 1923; 32, 318-9] and that of metallic cadmium described by T. Svedberg (*Rept. Farad. Soc. and Phys. Soc. Lond. on Phys. and Chem. of Colloids*, 1921). This is an instance of thixotropy.

Some of the colloid-chemical principles involved in intracellular changes are apparently the following:

*Gel formation* (pectization)—when the gel forms in certain localities, banded orientation (Liesegang's rings) and differential diffusion may occur in it.

*Re-solution* (peptization)—this may be consequent upon the action of enzymes released or activated by changes in H-ion concentration, which may follow differential diffusion. These

changes in H-ion (or other ion) concentration may also determine viscosity.

*Cumulative protection*—alteration of one of a connected series of protectors may produce important changes.

*Colloidal influence on crystallization tendencies*—astral rays seem indicative of this.

*Catalysis*, including enzyme action—(see pp. 39 and 334).

## GROWTH

For years it has been taught as an elementary distinction that non-living things grow by *accretion*, while living things grow by *intussusception*. Thus Huxley in his "Anatomy of Invertebrates" (page 10, 1888): "The increase in size, which constitutes growth, is the result of a process of molecular intussusception, and therefore differs altogether from the process of growth by accretion, which may be observed in crystals."

Considering the table of material units shown on pages 28-29, it will be at once evident that intussusception in a body of any upper order of complexity, is resolvable into accretion at the surface of particles of some lower order, while conversely, accretion at the surface of particles grouped to form a mass of a higher order of complexity, results in the growth of this mass by intussusception. All growth is thus, ultimately, accretional. (See paper by Alexander & Bridges, in Alexander's "Colloid Chemistry," Vol. II).

The fact that structures simulating organic growths can be produced by allowing precipitates to form in colloidal gels has long been known, and many beautiful experiments may be made along these lines.\* *Differential diffusion* through semi-permeable membranes, and the resulting osmotic pressure, are large factors in growth, to which must be added the formation of insoluble chemical compounds and, especially in organisms, the manifold effects of colloidal protection, coagulation, peptization, and adsorption. Thus Wislicenus showed that the *cambial or running sap* of trees in the spring is full of colloidal substances which

\* See R. E. Liesegang, "Kolloid-chemische Theorie des Lebens"; Stéphane Leduc, "Les Croissance Osmotique et l'Origine des Etres Vivantes"; A. L. Herrera (Mexico) has worked over thirty years on Plasmogeny. There are papers by all these scientists in Alexander's "Colloid Chemistry, Theoretical and Applied," Vol. II, 1928.

coagulate irreversibly after their adsorption by the wood cellulose (Lignification.) See p. 341.

The *punctum vegetationis* of plants is usually more acid than the balance of the plant (has a lower pH) and therefore tends to swell more and be more hydrous and tender—*e.g.*, in the case of asparagus. The lower and older leaves of plants generally wilt first on a very hot day.

The colloidal nature of the structures and catalysts with which food comes in contact directs and regulates the whole process of development. From the same soil we may produce a lily and a beet, a turnip and a rose. The same sap rising in a tree will produce one kind of fruit on some branches, but another kind on grafted branches made up of cells and tissues of another variety. From tiny cells almost undistinguishable from each other there develop the most diverse animals; yet compressed within that space are the differences in chemical constitution and colloidal structure that render possible and, in most cases, insure very tenaciously the close resemblance of offspring to parent.

Constructive and destructive processes are going on side by side in the organism, and, as R. S. Lillie puts it [Scientific Monthly, Feb., 1922], visible growth simply represents the accumulated excess of the former over the latter. Broadly, the constructive processes involve the formation of species-specific substances, including sols and gels, followed or accompanied by the formation of new compounds, aggregates, or precipitates in their presence, and then usually by a slow syneresis which produces most of the hardenings of old age. Chemically, there is much similarity, if not sameness, about the structures formed, which might point to a common evolutionary origin. Thus even cartilage, the precursor of bone, is allied to chitin of insects and the mucus of snails, for all yield chondroitin-sulphuric acid (A. P. Mathews, University of Cincinnati). But, physically, there are enormous differences in form, percentage of composition and function.

Colloidal sols and gels exert a powerful and specific influence on developing structures, as may be seen by allowing different salts and salt mixtures to crystallize in the presence of colloids such as gelatin or gum arabic, and also by allowing precipitates to form by diffusion in various jellies (gelatin, agar and silicic acid). See also p. 357.

## PLANTS

Plant tissues are likewise colloidal gels and sols, and as the sap which also contains colloids circulates and diffuses through them, each tissue selectively adsorbs and elaborates certain constituents. Thus, the starch-forming substances are fixed by the roots of the potato and tapioca, by the stem pith of the sago palm and by the seeds of cereals. Stems take up substances required for upward growth, roots those for downward growth.

"Wood is primarily the result of a colloid adsorption synthesis" (H. Wislicenus, in Alexander's "Colloid Chemistry," Vol. III, p. 67-74). The adsorbent is the "skeletal substance," the chemically passive micells of the cellular matrix, consisting largely of cellulose. The adsorbate is carried in by the cambial sap as a mixed hydrosol called "lignin," containing colloidal polysaccharides (pentosans, hexosans, hemicelluloses and wood gums), colloid calcium salts of pectinic acid and other plant acids of high molecular weight, and colloidal derivatives of polyoxybenzol and cymol (which condense to tannins, phlobaphenes, etc.). The spring or "running sap" is particularly rich in sugars, but from the middle of May until August the cambial sap is rich in the colloidal wood-forming substances which effect lignification.

The annual rings of trees offer certain possibilities as to the estimation of the age of the trees, the dating and relationship of past events, and the course of past weather conditions; for the quantity and richness of the cambial or "running" sap (see above) each spring, and subsequent growth during the summer, vary with the weather. In years favorable to tree growth, the annular rings are wider, while in years of drouth they are narrower. Prof. A. E. Douglass (Univ. of Arizona) by correlating tree-ring patterns of very old but still living trees with the rings of beams from the ruined pueblos of the Southwest, has established data pre-dating the landing of Columbus. Some of the giant Sequoias in California were living at the time of the Exodus (about 1,550 B.C.). Individual cells in the tree cactus and the redwood may live more than a century (for references see D. T. MacDougal and Gilbert M. Smith, *Science*, 1927, 66, 456-7. Also see D. T. MacDougal in Alexander's "Colloid Chemistry, Vol. II, Chem. Cat. Co., 1928).

## CHAPTER XIX

### GENETICS \*

GENETICS is a branch of biology which concerns itself with heredity and the mechanism of heredity. Its conclusions are mainly derived from careful observations on breeding results and the development of plants and animals. Geneticists have finally demonstrated the physical existence of *directive units of colloidal dimensions*, termed *genes*, which act as producers and differentiators of the heredity types and activities exhibited by members of the clan or family of individuals descended from an original ancestor or ancestors.

The basis of modern genetics was laid by Gregory Mendel, Abbot of Brnn, through breeding experiments which he carried out in his cloister garden. Working with the common garden pea (*Pisum sativum*), Mendel crossed a tall (T) with a dwarf (D) variety, and focussed his attention on the way in which these two characteristics were inherited by their various descendants. In the first family ( $F_1$ ) of hybrids (that is, plants growing from seeds of the first cross), *all members were tall*, there being none of dwarf or intermediate size.

*Mendel's First Law—Segregation.* On raising seeds from the  $F_1$  hybrids, Mendel found that the second family ( $F_2$ ) always gave an *average ratio* † of *three* tall to *one* dwarf. The  $F_2$  dwarfs always bred true, and so did one-third of the tall. The other two-thirds of the tall behaved like the original hybrids ( $F_1$ ), giving three tall to one dwarf in  $F_3$ . Mendel termed tallness the *dominant* character, while he called dwarfness the *recessive* character because it reappeared in subsequent generations raised from the hybrid type.

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\* Sincere thanks are due to Dr. Calvin B. Bridges (Carnegie Institution of Washington, Pasadena, Cal.) for critical suggestions and for illustrations. Dr. J. McKeen Cattell, Editor of Science, and The Scientific Monthly, also kindly gave permission for reproduction of figures, etc.

† Wherever we deal with calculations based on statistical averages, the more and more units we include in our observations, the more accurate our calculations will seem to be. But as we observe fewer and fewer units, the less and less accurate our calculations will seem, until with a single unit we would be merely guessing. Hence the importance, in genetic work, of considering a sufficient number of offspring if we expect to observe the application of Mendel's laws.

Mendel obtained similar results with several other pairs of alternative characters. The experimental results are epitomized in the subjoined table, where R indicates the recessive character, D indicates dominants which breed true, and *D* indicates dominants which throw the recessive type.

Family	Parents	D x R
F <sub>1</sub>		$\downarrow$ <i>D</i> $\downarrow$
F <sub>2</sub>	$\begin{array}{c} \overline{D} \quad D \quad D \quad R \\ \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \\ D \quad \overline{D} \quad D \quad D \quad R \quad \overline{D} \quad D \quad D \quad R \quad R \end{array}$	

Mendel showed that this *segregation*, giving 3 to 1 ratios, could be explained by assuming that the characters depended on discrete representative producers (which were later called genes). Each of the hybrids would develop under the joint control of a dominant and of a recessive gene (D/R) in every cell of its growing parts. When eggs and pollen are finally formed, these genes *segregate* (i.e., separate) from each other *cleanly*, so that each egg or each pollen grain gets a pure dominant (D) or, equally often, a pure recessive (R) gene. The table below shows how the 1:2:1 ratio of (D/D):(D/R):(R/R) progeny results from random or haphazard fertilizations with *equal numbers* of eggs and pollen grains of the two types.

Pollen .....	$\begin{array}{cc} D & R \\ \downarrow & \swarrow \\ & \searrow & \downarrow \\ D & & R \end{array}$
Eggs .....	
F <sub>2</sub> progeny	D/D:(D/R, D/R) : R/R

In order to put this hypothesis of equal numbers of pure-type germ-cells to test, Mendel fertilized the *dwarf* flowers with pollen from the F<sub>1</sub> hybrid flowers, and secured, as he had expected, tall- and dwarf-producing seeds in *equal numbers*. The reason is evident from the following diagram:

Eggs of pure recessive dwarf .....	$\begin{array}{cc} R & R \\ \downarrow & \swarrow \\ & \searrow & \downarrow \\ D & & R \end{array}$
Pollen of F <sub>1</sub> hybrid (tall) .....	
Test-cross progeny	(R/D, R/D) : (R/R, R/R) 2 tall                      2 dwarf



*Mendel's Second Law—Independent Assortment.* By crossing peas having *yellow and round* seeds with peas having *green and wrinkled* seeds, Mendel secured  $F_1$  seeds that were yellow and round, these characters being dominant over the recessive alternative characters green and wrinkled. But these  $F_1$  plants, when self-fertilized, gave seeds which showed the following four types in the ratio of 9:3:3:1—yellow round; yellow wrinkled; green round; green wrinkled. The explanation for these numerical results, Mendel assumed, is that the distribution of the segregated genes of the pair green versus yellow is independent of the distribution of the round and wrinkled segregants. Thus, there would be four equally numerous kinds of ova and four corresponding kinds of pollen grains, which, when uniting at random during fertilization, would give 16 different combinations in the ratio of 9:3:3:1 for the different visible types.

*Linkage.* Soon after the resurrection of Mendel's work, William Bateson and R. C. Punnett (Second Rept. Evolution Comm., Roy. Soc., London, 1905) reported experiments with sweet peas in which they found that the two factor-pairs purple versus red flower color and long versus round shape of pollen, did not assort at random. If "red" and "long" entered a cross together, they tended to remain together in subsequent generations in higher proportion than allowable for random assortment. This failure of random assortment is now known as *linkage*. Linkage is explained by the assumption that the genes of the two pairs which fail to assort at random, are discrete parts of the same carrier, namely, the *chromosome*, which is a "package" of genes arranged in line, somewhat like beads on a string.

*Crossing-over; Inversion; Translocation; Deficiency; Duplication.* These terms represent modes of "gene-shuffling" following patterns different from the usual random mixing of maternal and paternal chromosomes as wholes. *Crossing-over*, one of the commonest, occurs when the two chromosomes of a pair twist about each other in a stage of germ-cell formation. Single and double crossing-over are diagrammed in Fig. 29.

Where a gene-block breaks loose and comes back into its original chromosome with wrong ends united, we have an *inversion*. If the loose gene-block joins on to another chromosome, we have a *translocation*. If the loose gene block is lost entirely,

we have a *deficiency* or *deletion*, (Fig. 30.) Fig. 31, from Prof. T. H. Morgan's Nobel Lecture (The Scientific Monthly, July, 1935) shows how a terminal inversion has forced one end of a chromosome to turn backwards during synapsis or conjugation. Deficiency is exhibited in Fig. 32, lack of a gene-block causing an outward looping of the normal chromosome during conjugation. The tendency of like genes to set themselves opposite to each

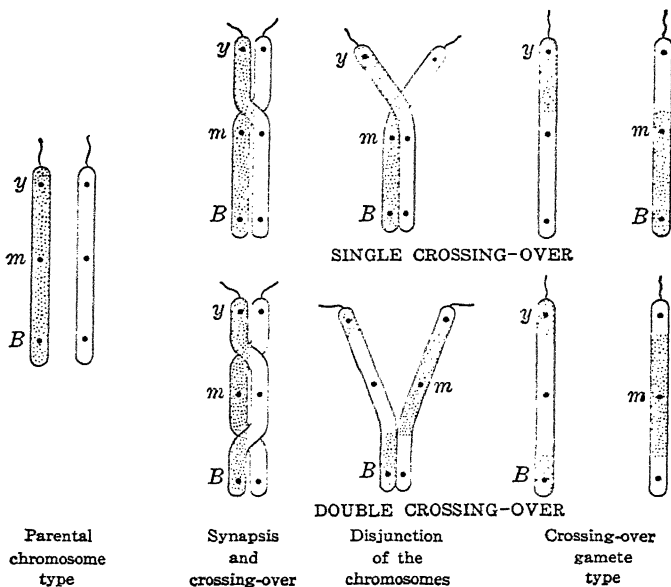


Fig. 29.

other, reminds one of the tendency of like molecules to assemble in a crystal lattice. C. B. Bridges has recently stated (Science, 1936, 83, 210) that the Bar gene (which causes reduced-eye) is a *duplication*, characteristic lines in the stained salivary gland chromosomes appearing twice.

Naturally, all these abnormalities in the relative positions or numbers of the colloidal cell catalysts, the genes, register various effects in the plant or animal. For example, in *Drosophila*, a deficiency in both chromosomes of the carrier pair is lethal; translocations may lead to intervarietal sterility. The chemical changes directed by the genes depend somewhat upon their position relative to other genes; for apart from the possible

influence of their electronic fields, this will govern their supply of "raw material," as is evident from the following simile of C. B. Bridges (from Chapter III on "The Genetics of Sex in *Drosophila*," in "Sex and Internal Secretions," edited by Dr. Edgar Allen) :

"Considered from the standpoint of its products, each gene is a chemical factory, devoted to the manufacture of a series of active chemicals and their delivery in sequence to the surrounding chromosomoplasm. Each of the genes in a given gene-string or chromosome has its own 'orders' to fill, and has the machinery

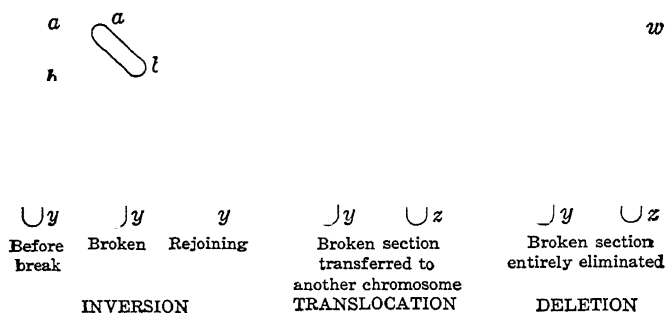


Fig. 30.

for producing its particular set of manufactured chemicals. A chromosome is like a row of factories set upon the bank of a canal, all delivering their goods by means of the waters of the canal, as well as helping themselves to raw materials brought by the canal."

*Drosophila melanogaster*. The speed of genetic experimentation was greatly increased by the use of the tiny yeast-eating fly, *Drosophila melanogaster*, which matures in about 10 days and has an adult life of over a month. About thirty or more prolific generations can be raised in a year in glass bottles in the laboratory, independent of weather conditions and at small cost. The breeding and crossing of strains is easily controlled.

The most extensive work with *Drosophila* has been done by Prof. T. H. Morgan (California Institute of Technology, Nobel Laureate) and his associates Calvin B. Bridges, A. H. Sturtevant, and H. J. Muller.

*Sex Determination.* Chromosomes of a predominant usual type are termed *autosomes* to distinguish them from the special one or more pairs of chromosomes whose segregation determines the sex of each offspring. The basic sex chromosome, termed the X-chromosome, has no discoverable mate in some species (known as XX-XO types), while in other species it has a mate, the Y chromosome (the XX-XY types). In one major group, includ-

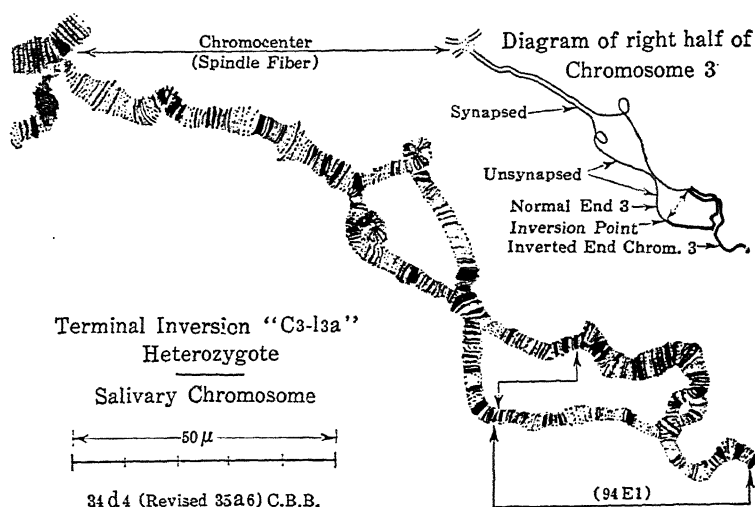
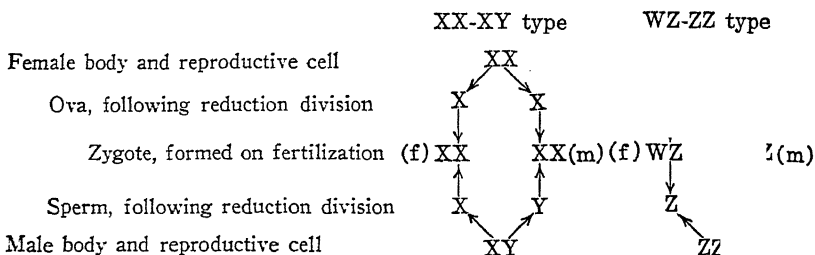


Fig. 31.

ing most insects and man, the female cells carry two X chromosomes, and the male only one, usually with a Y present. Man is of the XX-XY type, the Y chromosome in human sperm having been recently discovered.

In another group (birds and moths) the male has two like sex chromosomes (ZZ) and the female two unlike sex chromosomes (WZ), of which one member is the same as in the male. The following diagrams indicate how these microscopic gene-carrying units dominate the determination of sex. But it must be clearly understood that in sex-determination, as in all other cellular developments, *all the genes* exercise an influence. What finally emerges depends upon the net results of the catalytic actions of all the genes working together, a summation expressed by the

term *genic balance*. If the genic balance is too greatly disturbed, the biont (plant or animal) may die or fail to reproduce.



There are 48 chromosomes in the case of man, 24 coming from each parent; and these are illustrated in Fig. 33, after Evans and Swezy (H. M. Evans and O. Swezy, Mem. Univ. California, Vol. 9, No. 1 (1929)). Thanks are due the authors

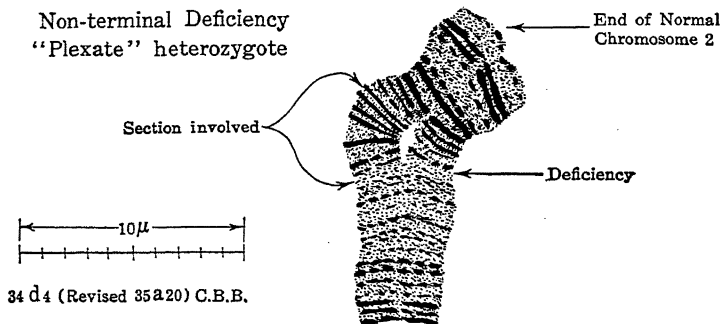


Fig. 32.

and the publisher for permission to reproduce this illustration. The chromosomes clump so quickly after death, that fixation of the cells in less than one minute was necessary. Operative cases and recently executed criminals furnished the specimens.

### *Changes in Genic Balance Consequent Upon Change in Chromosome Number*

It very occasionally happens, in the course of germ-cell formation, that the members of a pair of chromosomes fail to separate in reduction division; hence both of them pass into one of the new germ cells, which thus acquires two of this particular

kind of chromosome, while the other germ cell has none. This phenomenon was termed *non-disjunction* by Dr. C. B. Bridges, who observed it in the case of the X-chromosome in *Drosophila*. Ova of two new kinds were thereby formed: AXX, representing autosomes with two X chromosomes, and AO, representing the autosomes without any sex chromosome. Now the sperms of *Drosophila* are of two kinds, half having an X sex chromosome, the other half a Y. Therefore on fertilization with these abnormal sperms, these ova may give combinations of chromosomes represented by AAXXY, AAXXX, AAXO, AAYO. The results



Fig. 33. The 48 human chromosomes.

of these chromosome changes on the flies are given in the following table, which begins at the top with the normal chromosome combinations (the A, representing a set of autosomes, is double because sperm and ovum each contribute one set of autosomes to the zygote):

TABLE XXVII

Chromosomal Constitution	Sex of Individual
AAXY.....	Male, normal
AAXX.....	Female, normal
AAXXY.....	Female, giving abnormalities
AAXXX.....	"Super-female," abnormal
AAXO.....	Male, sterile
AAYO.....	Dies—sex?

These results indicate that the presence of an X chromosome is essential to development; that the presence of more than one X leads to a female; that the presence of a Y chromosome is needed to prevent sterility in a male, for without it the male fails to produce sperms which function.

Bridges further found flies in which the *number of autosomes* had become abnormal; they appeared in sets of three instead of in pairs as is usual. This can be clearly seen on microscopical examination of the cells, these *triploid* flies having a chromosomal

constitution expressed by AAAXXX. The viable offspring of triploids come from eggs of four types: AX, the usual *haploid* type; AXX and AAX, mixed type; and AAXX, the double-haploid or *diploid* type. (Also extra Y chromosomes may be present). Some of the results emerging when ova from a triploid fly were fertilized by normal sperm, are given in the table below:

TABLE XXVIII

Chromosomal Constitution	Sex of Individual
AAXY (normal diploid fly).....	Male, normal
AXXX ".....	Female, normal
AAAXXX (triploid).....	Female, producing abnormalities
AAAXX ".....	"Intersex," sterile
AAAXXY ".....	"Intersex," sterile
AAAXY ".....	"Super-male," sterile
AAXXX ".....	"Super-female," sterile

Here we see again the potent effects of the shifting of the genic balance through change in the chromosome number, and further proof that sex is not determined by the X-chromosomes alone, but that the X carries genes tending to produce female characteristics and the autosomes carry genes with male tendency, the combined action determining the sex.

Haploid individuals (they may be termed *haplonts*) occur in nature; *e.g.*, male bees, wasps, and ants have half the normal number of chromosomes, and haploid tobacco plants and Jimson or Jamestown weed (*Datura*) have been found.

Certain roses are *polyploids*, some having 56 chromosomes, which is 8 times the normal 7 of the basic rose type. This *polyploidy*, combined with extensive hybridization, has given an enormous variety of rose types, many of which do not produce viable seed but are propagated by cuttings or stolens. The earliest wheats utilized in the Neolithic period in Europe belonged to the Einkorn group, having normally 7 pairs of chromosomes (*Triticum monococcum*). Wheats of the Emmer group, with larger grains and 28 chromosomes, were grown in Egypt over 7,000 years ago, and were known to the Swiss lake-dwellers. In the Graeco-Roman period, in addition to these improved 28 chromosome wheats, there appeared the *Vulgare* group, with 42 chromosomes, to which most of our modern wheats belong. It is favored because of the large size of its grains. Observing people, everywhere and at all times, are keen to take advantage

of a natural phenomenon, even if they cannot fathom the underlying causes.

### *The Physical Reality of Colloidal Genes*

There is given in Fig. 34 the most recent "genetic map" of the three autosomes and the X chromosome of *Drosophila melanogaster*, prepared by Dr. Calvin B. Bridges, showing the linear order and relative spacing of the best known genes. The special gene names refer to the various recognisable mutant characteristics in the flies. Taking advantage of proven tendencies for the "crossing-over" of blocks of genes, and by careful selection of parents, geneticists can "synthesize" flies of any desired genetic constitution, somewhat as organic chemists can synthesize organic molecules.\*

These gene-strings correspond to the cytologist's four pairs of chromosomes, and in them the following genetic factors have been located:

*Chromosome 1*—about 150 sex-linked characters, involving size, shape, and color of eye: shape and veining of wings; body color; hairs and spines.

*Chromosome 2*—about 120 diverse body changes.

*Chromosome 3*—about 130 other body changes.

*Chromosome 4*—about 10 body changes, including eye-size (and no eye), reduction of hair size, mode of carrying wings.

Further microscopic evidence of the physical reality of the genes, which are so small as to approximate colloidal or large molecular dimensions, was given when Prof. T. S. Painter (University of Texas) showed that their locations could be definitely ascertained in the chromosomes of the salivary gland cells of *Drosophila* (Science, Dec. 22nd, 1933; Jour. Heredity, Dec.,

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\* Dr. D. M. Wrinch (Oxford University) has advanced the view that chromosomes consist of protamine molecules lying helically along a quasi-cylindrical surface, the genetic nature of the chromosome residing in a characteristic arrangement of amino acid residues of various types. The "dark bands" on the salivary gland chromosomes are interpreted as regions of high density of nucleic acid or of basic amino acid residues. "Our hypothesis suggests that a gene may be associated with a length as small as 3.5 angstrom units." (Proc. Int. Congress of Botany, Amsterdam, 1935, 2, 24; Nature, 1934, 134, 978; 1936, 137, 411; Protoplasma, 1936, 25, 550-569).



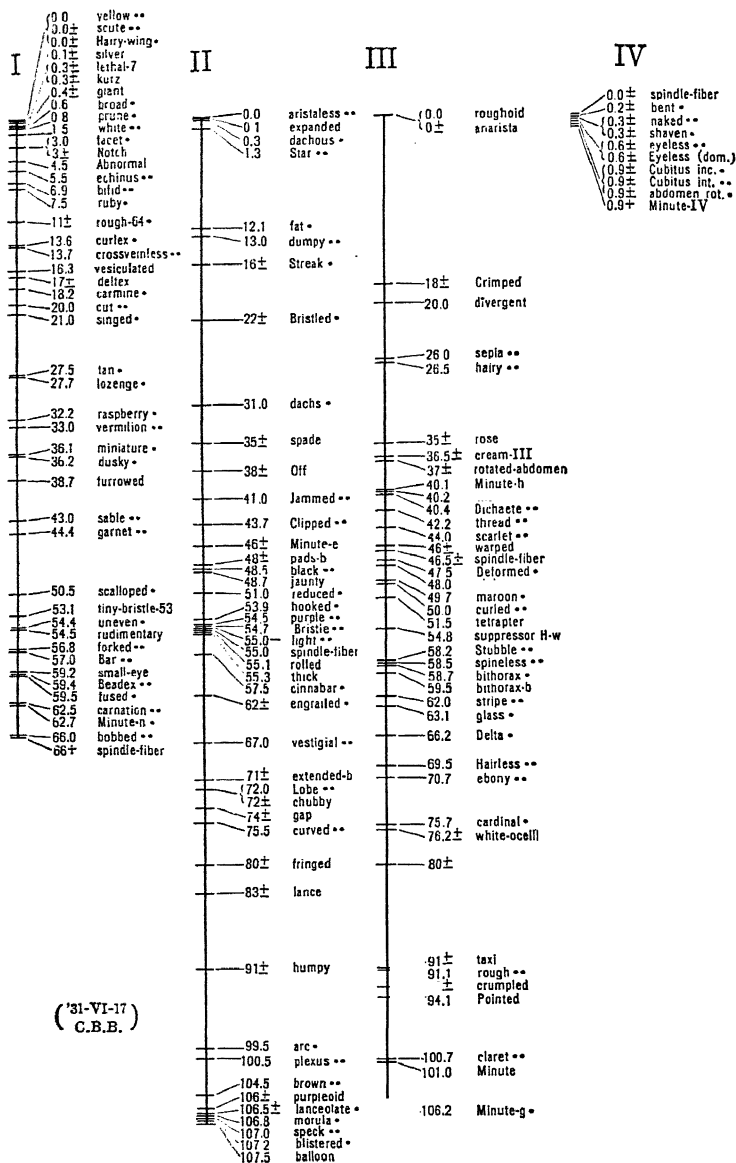


Fig. 34. Genic map of the four chromosomes of *Drosophila melanogaster*, showing the linear order and distance apart of the genes (after C. B. Bridges).

1934). These chromosomes may be stretched to about 175 times the length of the chromosomes in sperm or ova. Characteristic structural bands are microscopically demonstrable, constituting a "genetic spectrum" which matches precisely with the genetic characteristics of the flies, as indicated in the chromosome maps. When, through "deficiencies," flies were bred without a certain character, examination of the salivary chromosomes showed that the bands associated with these characters were missing. Bridges has published (see *J. Heredity*, Feb., 1935) greatly enlarged illustrations of the four salivary chromosomes of *Drosophila*,

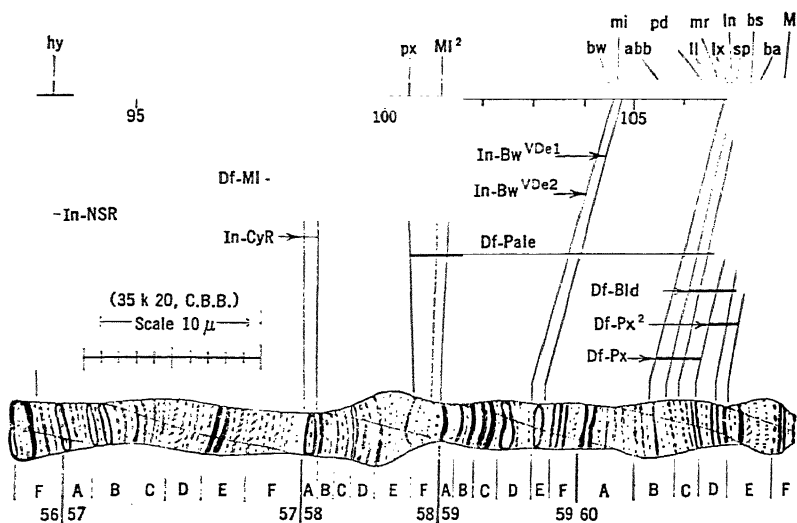


Fig. 35. Section of right end of second chromosome (salivary gland of *Drosophila melanogaster*) with corresponding portion of chromosome map (after C. B. Bridges).

against which are matched the chromosome maps previously worked out. He has kindly supplied Fig. 35, which shows a small section of the right end of the second chromosome, with a corresponding portion of the map. In the upper right-hand corner of Fig. 36, are shown the four pairs of chromosomes of *Drosophila* at the magnification indicated by the accompanying scale. The main portion of the figure gives, in the same magnification, the smallest two chromosomes from a salivary gland cell in the metaphase stage (see p. 337).

*Gene Changes Caused by X-rays*

One other item of surpassing interest must be given. In 1927 Prof. H. J. Muller (University of Texas) reported the artificial transmutation of the gene (Science, 1927, 66, 84-87). On treating *Drosophila* with proper doses of filtered X-rays, he found that although many individuals were killed or rendered sterile, nevertheless some survived and a surprisingly high proportion of their children showed *new and heritable characteristics*. This method has since been extensively used to produce mutant forms of many plants and animals.\*

It had long been known that in nature there may suddenly

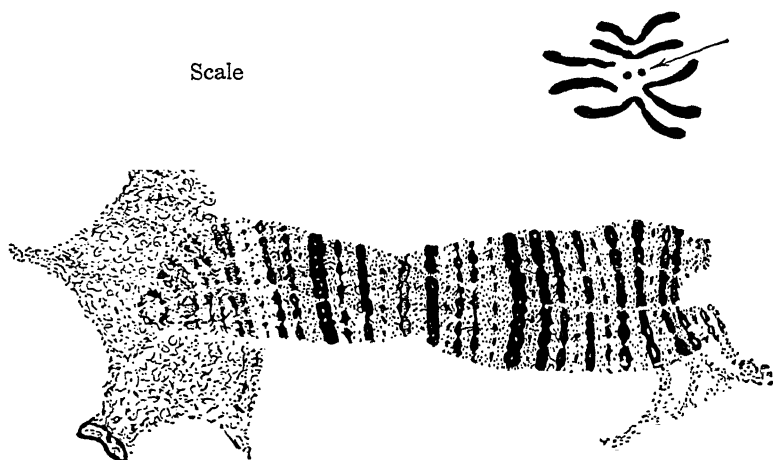


Fig. 36. Salivary gland chromosome from *Drosophila melanogaster*.

appear a new heritable type, termed a *sport* or *mutation*. For example, the orange, originally a native of Asia, has been introduced into many other lands. Among the orange trees in Brazil there appeared a sport or mutant giving navel oranges. Since viable seeds were not produced, the peculiar plant was propagated by grafting, and one of the grafted plants was sent to Washington, D. C., whence it became the non-sexual "ancestor" of the immense number of navel orange trees in California, even though in a state of nature such a sport would have had no descendants.

\* N. W. Timoféeff-Ressovsky, K. G. Zimmer and W. Delbrück (Nachr. Gesell. Wies. Göttingen, New Series, 1935, 1, 189-245) give a theoretical discussion on the nature of gene mutation and gene structure, especially as affected by radiation.

Muller's discovery led to the view that perhaps some natural source of X-rays or similar radiation (*e.g.*, cosmic rays) might be partly responsible for the spontaneous rare mutations in nature, for this rate was somewhat increased in seeds grown where such radiation was more intense. But Muller's direct radiation method speeded up the natural mutation rate about 15,000 per cent. While some of the effects of radiation are gross changes in the chromosomes (*e.g.*, deficiencies, translocations), in most cases there seems to be an actual chemical or physicochemical alteration in the still smaller colloidal genes.\* If such heritable gene or chromosome changes result in the development of a line of plants or animals which has advantages over others in the struggle for existence, such new lines would tend to replace, or at least to develop along with, existing lines, thus providing changes which are effective in evolution.

#### SOME FACTORS INFLUENCING DEVELOPMENT

It is the general rule in biology that descendants resemble parents, and that a parent organism cannot pass on to offspring a factor which the parent did not receive from the germ-plasm † of its immediate progenitors. Many apparent exceptions to this general rule have been traced to the existence in the parent gametes of recessive factors, which, while suppressed in the parent, may be liberated again in the offspring. Whether we accept the view of Darwin that large differences can represent the summation of small differences, or the more probable view of Bateson and others, that mutation or variation is a definite physiological event, some explanation must be given as to the origin or source of these exceptions to the general rule of resemblance, for they constitute the steps by which evolution haltingly proceeds.

The crying need that we must find a chemical, physical or physico-chemical basis for mutation or variation has been voiced by many.‡ Thus in his address before the British Association for the Advancement of Science (Australia, 1914, reprinted in *Smithsonian Report*, 1915, pp. 359-394), Sir William Bateson said:

\* This brings to mind the fact that ergosterol (and its congeners, according to recent work) does not function as "vitamin D" until after exposure to radiation.

† This includes both the chromosomes and the cytoplasm.

‡ Such an explanation is suggested on pp. 368 *et seq.*

"Every theory of evolution must be such as to accord with the facts of physics and chemistry, a primary necessity to which our predecessors paid small heed. . . . Of the physics and chemistry of life we know next to nothing. Somehow the characters of living things are bound up in properties of colloids, and are largely determined by the chemical powers of enzymes, but the study of these classes of matter has only just begun. Living things are found by simple experiment to have powers undreamt of, and who knows what may be behind?"

In nature, both animate and inanimate, the following basic factors tend to produce *symmetrical orientation or aggregation*: (1) Crystallization and orientation in surfaces; (2) Diffusion, as in the formation of Liesegang's rings, agate, etc.; (3) Electric or magnetic fields of force; (4) Harmonious vibration as of air, water, or the interesting vibration patterns known as "Chladni's figures" after E. F. F. Chladni (1756-1827). We here disregard mere chance and the conscious arrangement by man.

The main factors modifying the crystallization of pure substances are: (1) Concentration; of solutes and ions (2) Temperature, including speed of chilling; (3) Pressure; (4) Agitation; (5) The presence of other substances, especially of colloids, which may profoundly modify crystal forms by protective action; (6) Iso-colloidism. Some substances have the power of interfering with their own crystallization, because a portion, which first reaches the colloidal state, then protects the balance.

Deviations from normal crystalline forms produced by the presence of colloids are usually symmetrical, but may not appear crystalline. Changes in the nature or degree of dispersion of the colloid, or in its percentage, mixtures of colloids, variations in salt or H-ion concentration of the solution, must all have an effect on the resultant quasi-crystals. Enzymes may, of course, entirely change the nature of the colloid. The species-specificity of proteins seems to be maintained by degenerating food protein to simpler forms (polypeptids and amino-acids) and then building up the specific proteins from these.

Among the factors influencing diffusion, especially in gels, are the chemical nature and particle size of the gel, and the concentration and nature of the diffusing solution, as well as its effect on the gel, membrane or tissues, and the permeability changes thus produced. In his chapter on "Growth, Metamorphoses and De-

velopment," Bechhold ("Colloids in Biology and Medicine," trans. by J. G. M. Bullowa, p. 252 *et seq.*, D. Van Nostrand Co., 1920) refers to some of the remarkable diffusion figures and osmotic forms\* produced by F. E. Runge and by Stéphane Leduc, some of which resemble algæ, fungi, seaweed, etc., and even show a cellular microstructure. While pointing out the great differences between these formations and the organized structures they simulate, Bechhold says: "The physical forces which produced these inorganic formations are the same as those which produce the growth and configuration of organized material membranes—osmotic pressure, diffusion."

Perhaps the most familiar instance of modified crystallization is to be found in the delicate frost tracery on window panes, the forms being probably influenced by the glass (itself a colloid) or by substances adsorbed at its surface. See, *e.g.*, the figures given by Wilson J. Bentley in "Monthly Weather Rev." 1907; also paper by Prof. Howard T. Barnes in Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied." A pioneer worker was Dr. Wm. A. Ord, whose book, "The Effect of Colloids on Crystalline Form and Cohesion," was published in 1879, too far in advance of its time to be appreciated. The writer has pointed out the powerful influence exerted by colloids such as gelatin, gum arabic and albumin on crystallization (Kolloid Zeit., 1909, 4, 86), and R. E. Liesegang, looking at the question from the opposite standpoint, has described the power of crystalloids to give a form to colloidal jellies (Kolloid Zeit., 1910, 7, 96). It may be said that with different salts or combinations of salts, various colloids or combinations of colloids, and variations in concentrations, temperature and speed of evaporation, will produce characteristic and generally reproducible forms on a microscope slide. A characteristic form of sodium chloride is a four-pointed star with fern-like arms which cross at a slight angle.

A few slides made with solutions of common salts such as NaCl, MgSO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, etc., containing from 0.5 to 50 per cent. of gum arabic or gelatin (figured on the basis of the dry salt), will illustrate what is meant. When a drop of the mixed solution is allowed to dry on the slide without cover glass, changes of concentration and temperature occur, giving a field that changes

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\* A. L. Herrera (Mexico) has devoted many years to these studies.

progressively from rim to center of the drop.\* A solution of one part sodium chloride, one part sodium carbonate (dry) and one tenth part gum arabic or gelatin in ten parts of water, when dried, shows in some part of the field a "flowering plant," with graceful stems and characteristic four-petaled flowers.

To see that a marked change may be produced by modifying the colloidal state of the protective substance, a slide was made with a solution containing egg albumen as the colloid. The solution was then heated until the albumen began to show a milki-ness, another slide was made, and after drying was compared with the first unheated specimen. The difference in crystalliza-tion was considerable.

Unusual crystalline forms, such as sphero-crystals and sheaf-life groups which are so often seen in the crystals of substances derived from organisms, are very often consequent upon the protective action of some colloid from which they are not entirely purified. Another curious occurrence must be mentioned here, which may be termed *auto-protection* because it is due to iso-colloidism. Before reaching the ordinary visibly crystalline state, particles of every substance must pass through the colloidal zone, and the particles first reaching that state may interfere with the normal crystallization of the rest. Thus ammonium salts, even without the addition of protective colloids, are prone to assume feathery or fern-like forms. The phenomenon is marked in the oleates and is probably the underlying cause of the formation of myelins, although their formation is fostered by such lipid protectors as cholesterin. According to J. G. Adami (Harvey Society Lecture, 1906), if certain simple soaps be dissolved by warming on a slide with water and then allowed to cool, they may show upon examination in the polarizing microscope a perfect rain of doubly refracting spherules, which, depending on the nature of the soap, may last for hours or days or else immediately give place to a brilliant white layer of formed crystalline plates. W. B. Hardy, E. Hatschek and others have described substances which form unstable gels that soon become crystalline.

Phenomena of this type may be due to auto-protection (p. 157), to successive steps in crystallization (p. 95), or to the emer-

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\* These are referred to by P. Lecomte du Nouÿ in his A.C.S. Monograph "Surface Equilibria of Biological and Organic Colloids" (Chem. Cat. Co., 1926); also in his paper in Vol. II of Alexander's Colloid Chemistry (Chem. Cat. Co., 1928).

gence of mesomorphic states (p. 98). G. Friedel considers O. Lehmann's "fluid crystals" as examples of the mesomorphic condition.

The bio-colloids are so readily affected by salts, H-ion concentration (effective reaction), temperature, actinic (sun's rays) and traumatic (shaking, mechanical injury) effects, that it is more surprising that plants and animals should breed true than that they should show variations. Therefore, although individuals may be much affected by such changes during their lives, it is evidently a rare occurrence that these changes are registered in the germ plasm by which alone they may be transmitted to offspring. The specificity of the germ plasm is evidently guarded by many factors, among which seem to be selective adsorption and differential diffusion of dissolved substances through its protecting walls or membranes. Nevertheless unusual influences must occasionally change it materially without destroying it, and along this line experiment may be directed.\* It may be that the germ plasm can be affected through the somatoplasm, as well as by direct means. And of all the variations, in nature only the beneficial changes survive.

Prof. Leo Loeb (Washington University) points out that *tissue formation* is probably due to factors analogous to those which cause the agglutination or flocculation of amoebocytes, a change which would also cause a clotting or thrombosis in the blood vessels. He regards the primary changes underlying these conditions to be localized alterations in colloidal state of certain constituents of the cells, probably of protein nature (see his paper in Alexander's "Colloid Chemistry," Vol. II, pp. 487-514, with extensive references). The development of organized vessels in cultures of blood cells has been described by R. C. Parker (Rockefeller Inst. for Med. Res.; Science, 1933, 77, 544-46), who concludes that isolated blood cells, in a plasma substratum, are capable of constructing highly organized channels that are analogous to the blood capillaries of the organism. The walls of the tubules first formed very shortly after the coagulation of the medium, develop as a result of the activity of living cells, or cell products, the so-called thrombocytes, which often are seen to spin out threads which bind together agglutinated masses.

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\* Since this was written, mutations have been experimentally produced by X-rays. See p. 354.



## CHAPTER XX

### HORMONES, VITAMINS—LIFE, DISEASE

HORMONES and vitamins are considered together because they both represent substances whose presence in minute amounts is essential to the normality of development and function in plants and animals. Hormones, sometimes referred to as "endocrines," *are produced within the organism*, many of them by glands or organs which discharge into the blood or other circulating fluid and which are often called "glands of internal secretion." The isolation, identification, and synthesis of many of the hormones and vitamins mark high spots in chemical research and have led to Nobel prize awards in chemistry and medicine in several cases. C. Eijkman did his pioneer work in Java on polished rice as a cause of beri-beri in 1890-1897; and Profs. E. H. Starling and Wm. Bayliss (University of London) coined the word "hormone" in 1902. Vitamins or their precursors occur in foods and *are produced outside the organism*. Casimir Funk coined the word "vitamine" in 1911.

Apart from their great interest, brief reference to hormones and vitamins is made here because their peculiar actions may, in some cases at least, prove to be due to their modification of biocatalysts or surfaces or to the production of changes in the permeability of tissues or membranes. Such mechanisms would permit minute amounts of materials to exert a profound influence on metabolism and function. Thus Prof. A. J. Clark (Chemistry and Industry, 1930, 49, 533-4) points out that the spindle-shaped cell of the frog's heart measures about  $130 \times 10 \mu$ , with a volume of about  $3400 \mu^3$ , while the molecule of acetylcholine has a diameter of about  $1.5 m\mu$ . Now Loewi showed that the nerves of the vagus reduce heart action by liberating acetylcholine around the heart cells, and Clark estimates that a few thousand of these molecules are sufficient to depress a single cell. "The relation in size is similar to that between a large whale (100 tons) and

a midge (1/3 mg.).” Prof. Reid Hunt (Harvard University) states that his data on this potent hormone may be expressed thus: 1 grain (originally the weight of a single grain of wheat) will suffice to lower the blood-pressure of a thousand million cats, but this dosage might not kill a single cat (Science, 1930, 72, 528). One part of adrenaline in a thousand million can produce a visible effect on the isolated gut of the rabbit.

Plants are greatly affected by minute amounts of specific substances. Growth-stimulating substances elaborated within the plant are termed *auxines*. F. Kögl, J. Haagen-Smit, and H. Erxleben (Zeit. physiol. Chem. 1934, 228, 90) found that  $\beta$ -indolyl-acetic acid acts as an auxine. Vitamin C promotes plant growth, and the prolan fraction from the urine of pregnant women greatly stimulates the growth of seeds. A. Winterstein reports that a crystallizate from the urine of pregnant mares is more active than the international standard estrogenic hormone, and estimates that 30-40% of the activity is due to accessory-hormones. (Chemistry and Industry, 1936, 55, 237.)

An interesting linking of auxines with genetic factors has just been pointed out. Dr. F. W. Went had shown that the buds and leaves of the corn plant produce a substance essential for growth of the stem, and the existence of a gene responsible for “dwarf” corn had long been known. Dr. J. Van Overbeek finds that this dwarf-determining gene acts by directing the formation of a relatively large amount of an oxidizing enzyme, which, in turn, destroys a relatively large amount of the growth-producing auxine. Dwarf mutations are known in the guinea pig (I. B. J. Sollas, Rep. Evol. Comm. Roy. Soc., 1909, 5, 51), and in the mouse (G. D. Snell, Proc. Nat. Acad. Sci., 1929, 15, 733) and are believed to act through creation of a working deficiency in the growth-promoting hormone of the pituitary.

Arttuturi I. Virtanen (Address to the British Assn. Adv. Sci., Chem. and Ind., 1935, 54, 1015) concludes that “although plants can be grown in sterile nutrient solutions containing no organic substances, their growth is markedly improved through the addition of very small amounts of certain organic compounds, part of which are important catalysts also in soil metabolism.” Inoculated legumes, grown in sterile quartz, excreted nitrogen compounds with over 87% of amino acids, of which about 50% was

aspartic acid and 45% a diamino acid, probably lysine. "The use of associated cultures offers great possibilities for the practical agriculturist. In this respect particular attention must be paid, besides, to the choice of suitable plant species, also the ratio of legumes to non-legumes." The use of clover as a "green manure" has long been known, and the expression "in clover" means to be in luxury or abundance.

Prof. Roger J. Williams (Oregon State College) recently reported the isolation of pantothenic acid, which he believes to be essential for the growth and respiration of living cells; and (with E. Rohrman) he reports that synthetic  $\beta$ -alanine is highly potent as an agent for stimulating yeast growth, and "has made it possible for the first time in history to grow yeast rapidly from a small seeding on a medium containing only well-recognized pure chemicals." (J. Am. Chem. Soc., 1936, 58, 695.) This latter material is highly effective, 1 part to 12 millions. Evidently many substances may act the part of "bios", an essential to yeast growth, reported many years ago. Prof. Effront (Brussels) long ago reported that diastases worked much better in the presence of small amounts of asparagin.

Experimentally, traces of many substances are able to cause a downward bending (*epinasty*) of the leaf-stalk (petiole) of the potato; *e.g.*, substances arising, probably by volatilization, from geranium petals; lily anthers; unripe apples, tomato, and squash; leaves of onion, lettuce, Virginia creeper; roots of radish, beet, turnip. (See F. G. Denny, Contrib. Boyce Thompson Inst., 1935, 7, 341-7.) Large use is now made of ethylene to develop the desirable color of citrus fruits (oranges, lemons, grapefruit), and ethylene chlorhydrin will cause potatoes to start growth without waiting over a "dormant" period. It seems probable that these substances act by their influence on catalysts, speeding up changes which otherwise go on slowly.

In order to economize space, only tabulated resumés are given of the hormones and the vitamins, and it must be understood that this information will have to be modified or extended in the light of later work.

Fig. 37, based on a color plate in Therapeutic Notes for April, 1935, produced by courtesy of Parke, Davis & Company, shows

some of the known endocrine relations which caused the pituitary to be dubbed "the director of the endocrine orchestra."

An interesting illustration of endocrine inter-relation appeared with a diabetic who had taken his morning injection of insulin without sufficient carbohydrate. On the way to his office, he felt the oncome of the effects of hypoglycemia (which may

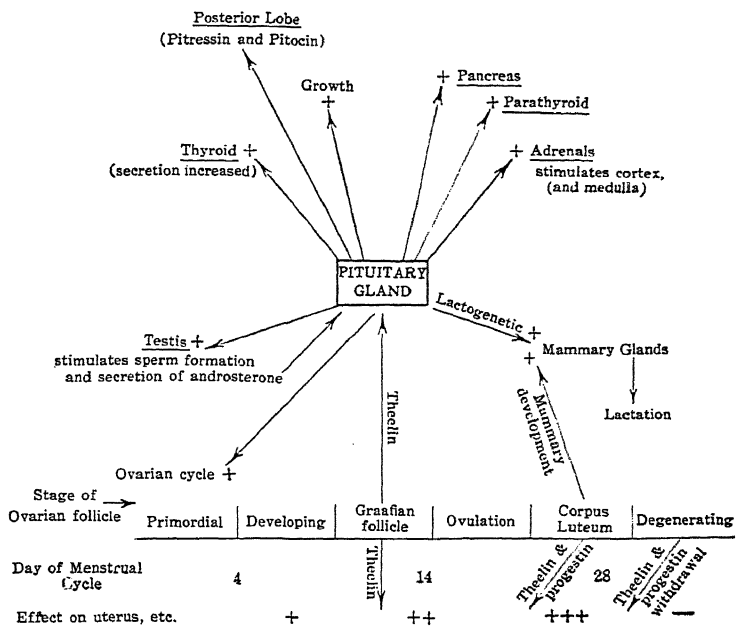


Fig. 37. Diagram showing some Endocrine, or Hormone, Inter-relations.

lead to convulsions and coma), and having been forewarned by his physician, hurried to the nearest store where he could purchase some sweet, like a chocolate bar. By the time he reached the store, he was incoherent, though conscious; and the shop keeper, thinking he was drunk, threw him out. His intense anger at such treatment led to an outpouring of adrenalin and the mobilization of his scant carbohydrate reserves, sufficient to bring him back to normality; whereupon he went to another store and purchased what was, for him, a life-saving sweet. (J. B. Collip.)

TABLE XXIX  
HORMONES\*

Source	Designation	Chief Physiological Effect	Unbalanced Supply May Lead to
<i>Thyroid</i> (1-e)	Thyroxine	Speeds metabolism, especially oxidation	+Exophthalmic goiter (Graves' disease) -Myxedema; infantile cretinism
<i>Parathyroids</i> (2-c)		Governs calcium metabolism	+Hypercalcemia -Tetany
<i>Adrenals</i> Medulla (1-e)	Epinephrine (Adrenaline)	Vasoconstrictor; raises blood-pressure	+High blood pressure; excitement -Low pressure; weakness Addison's disease
Cortex (3-c)	Cortin		
<i>Pancreas</i> (Islands of Langerhans) (2-d)	Insulin	Controls sugar oxidation and storage	+Hypoglycemia -Diabetes mellitus
<i>Pineal Gland</i> (a)			
<i>Thymus Gland</i> (a)			
<i>Intestinal Tract</i> Stomach (d) Duodenum (b)	Gastrin Secretin	Stimulates gastric secretion; increases flow of pancreatic juice Makes bile flow	
<i>Pituitary</i>	Choleocystokinin		
Posterior (2-d)	α hypopharmine (Pitocin) β hypopharmine (Pitressin)	Oxytotic; retards water elimination Increases blood pressure	-Diabetes insipidus
Anterior (2-b)	Adrenal-affecting " " Pancreas- " " Parathyroid " " Fat-metabolising	affects fat metabolism affects carbohydrate metabolism	
	Diabetes-producing		
	Gonad-stimulating " " Thyroid- " " Milk-producing (Prolactin)	(Prolan A and B) Lactation	
(c)	Growth-promoting		+Acromegaly (giantism) -Cachexia (Simond's disease)
	Luteinizing	On ovary & testes	

TABLE XXIX—HORMONES (*Continued*)

Source	Designation	Chief Physiological Effect	Unbalanced Supply Leads to
<i>Ovary</i> (d)	Theelin (folliculin, estrin)	Estrus	
<i>Corpus Luteum</i> (3-e)	Theelol Progestin Theelin	Prepares uterus	
<i>Testes</i> (2-e)	Testosterone Androsterone	Develop secondary male characteristics	
<i>Nerves</i>			
Parasympathetic	Acetylcholine	Quiets smooth muscle	
Sympathetic	Sympathin	Excites smooth muscle	

The *phases of research* concerning the several hormones are indicated thus:

- |                      |                                      |
|----------------------|--------------------------------------|
| (a) predemonstration | (d) isolation and analysis           |
| (b) demonstration    | (e) synthesis of identified compound |
| (c) concentration    |                                      |

The probable (or proven) chemical nature of the several hormones, where information exists) is indicated thus:

- (1) Simple basic compounds and aminoacid types
- (2) Peptone or peptide type
- (3) Lipoidal type (no nitrogen)

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\* Thanks are due to Dr. Oliver Kamm (Parke, Davis & Co.) and to Prof. I. Greenwald (N. Y. University) for information supplied.

TABLE XXX—VITAMINS\*

Designation	Properties	Main Effects of Deprivation	Good Food Sources	Chemical Nature
A—Anti-ophthalmic	Fat-soluble Oxidizable	Xerophthalmia Night-blindness Stunted growth	Fish oils, liver, fresh vegetables, egg-yolk, butter, cream	$C_{40}H_{56}O$ , derived from various carotenes which serve as precursors (P. Karrer)
B ( $B_1$ )—Anti-neuritic	Water-soluble Relatively heatlabile, especially in alkaline solution	Beri-beri (in man) Polyneuritis (in rats) Loss of appetite	Wheat, eggs, yeast, milk, fruit, vegetables	$C_{12}H_{16}N_4O_8S_2$ HCl (hydrochloride of base) (R. R. Williams)
C—Anti-scorbutic	Water-soluble Oxidizable Hurt by heat	Scurvy Fatigue Soft gums	Citrus fruits, peppers, spinach, water-cress	$C_6H_8O_6$ , ascorbic or cevitamic acid (A. Szent-Györgyi)
D—Anti-rachitic	Fat-soluble Resists heat well, oxidation fairly well	Rickets	Fish liver oils, eggs, milk. Sunlight for irradiation	$C_{27}H_{44}O$ , OH, ergosterol, one precursor, transformed into the vitamin on irradiation, presumably by intramolecular rearrangement (A. Windaus)
E—Anti-sterility	Fat-soluble Resists heat, but not oxidation	Sterility (in rats) Organic degeneration in male; lack of placental formation in female	Wheat, milk, eggs, meat, lettuce, water-cress	
G ( $B_7$ )†—Anti-pellagric	Water-soluble Relatively heat-stable	Pellagra Skin, digestive nervous troubles	Eggs, milk, and vegetables, yeast, liver	$C_{17}H_{19}O_4N_4$ , lactoflavine (R. Kuhn)

\* Thanks are due to Prof. B. Harrow (C.C.N.Y.) for critical suggestions.

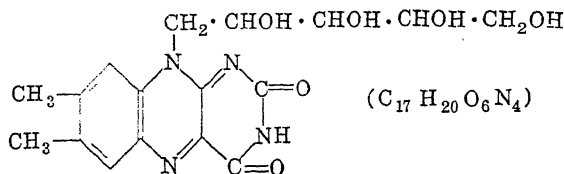
† This is a group of substances of which only lactoflavine has been identified. A certain amount of unsaturated fatty acids (linolic, linolenic) appear to be food essentials, and are by some termed Vitamin F.





Vitamin E—Structural formula not yet elucidated. Probably a higher alcohol, tocopherol (Evans).

Vitamin G ( $B_2$ ) (Lactoflavin) :



### PHYSICO-CHEMICAL DETERMINATION IN LIFE AND DISEASE\*

Broadly viewed, the most striking phenomenon exhibited by living units is the general uniformity, among members of various and widely differing races or clans, in composition, structure, development and reproduction. Many kinds of deviations from normality (*e.g.*, individual idiosyncrasies, disease, evolution of new types), demand explanation; but still more urgent is the necessity of considering the basic principles whereby normality is established. Despite differences in food and surrounding conditions, the fundamental life processes of most living beings are unerringly shepherded along definite paths and sequences, so that plants and animals breed true to type. Like the Norns of Norse mythology, genes weave the chemical warp of life into the woof of the milieu.

The law of probability, the biological and evolutionary data, and especially the demonstration of the existence of living units of ultramicroscopic dimensions (*e.g.*, bacteriophage, filterable viruses, mosaics), favor the view that life began in the molecular or near-molecular range and developed centrifugally in complexity, giving rise to the "box-within-box" structure found in both plants and animals. Thus the genes of near-molecular size were aggregated into groups or strings (the chromonemata), which, when surrounded by substances in process, established an interface against the milieu and became evident as chromosomes. Chromosomes were, in turn, surrounded by material which developed the karyon or nucleus, and this became surrounded by a pool of cytoplasm which established an interfacial cell wall. Development

\* Alexander, J., *J. of Heredity*, 1936, 27, 139-150.

of multicellular from monocellular organisms could have then followed.

The chance of the spontaneous origin of an elephant, a mouse, or even of an ameba, is practically nil. The simpler the unit, the greater the probability of the chance assemblage of its constituent atoms and molecules into its particular pattern. The simplest conceivable living unit would be the hypothetical "moleculobiont," \* a molecule capable of catalytically directing chemical change and at the same time capable of directing its own duplication. To put it concisely, such a unit is an *autocatalytic catalyst*. The primitive biont must have possessed the ability to live, to develop, and to reproduce on non-living nutrients, as do the well-recognized group of autotrophic organisms which are of such great importance in the formation and fertility of soils (*e.g.*, *Nitrosomas*, *Nitrosococcus*, *Nitrobacter*, *Thiobacillus*).

While spontaneous generation may now be continually occurring, any new unit would run slight chance of recognition, because of its ultramicroscopic size and unpredictable emergence, and it would have but slight chance of surviving to establish a new race or clan, in the face of the attack and competition of numerous predatory and well-established forms.

### *Enzymes—Organic Catalysts*

With primal organisms, gene-like units were in all probability the sole dominators of life processes. In higher forms, we find a great variety of specific secondary catalysts, termed enzymes, incapable of self-reproduction, whose formation has been in some manner directed by the truly living, self-reproducing units. Efficient enzymes come into existence when smaller sub-units (atoms, ions, molecules, or colloidal particles) unite to form larger, but not too large, particles having an extensive exposure of specifically active electronic areas, and not too high a particulate kinetic activity. These essential conditions may be met either by the formation of chemical molecules of colloidal dimensions, or by the absorption of specific units by colloidal particles in such orientation that a specifically active electronic area develops. Once formed and retained in active state, enzymic cata-

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\* Alexander, J., and C. B. Bridges. "Some Physico-Chemical Aspects of Life, Mutation, and Evolution," in Vol. II of *Colloid Chemistry*. 1928 (Chemical Catalog Co.).

lysts can add much to the chemical capabilities and complexities of the biont (living unit).

G. Bredig,\* by adding amino groups to fibers (cellulose, wool, silk), produced catalysts which split off CO<sub>2</sub> from bromcampho-carbonic acid. The work of Richard Kuhn, Otto Warburg, and their collaborators † indicates that the water-soluble lyochromes, the flavines,‡ which apparently constitute vitamin B<sub>2</sub> (termed vitamin G by American chemists), exhibit enzymic activity when brought into the colloidal state, presumably by fixation on a colloidal carrier, yielding the yellow oxidation enzyme of Warburg. Kuhn gives the following table:

TABLE XXXI

	Solubility in			Activity as	
	Dialysis	Water	Chloro- form	Vitamin	Enzyme
1. Flavoproteins					
Flavo-polysaccharides	—	+	—	+	+
2. Flavines.....	+	+	—	+	—
3. Irradiated Flavines...	+	+	+		

Richard Willstätter§ has proposed the term "symplex" for compounds where high-molecular substances are bound by residual valencies, *e.g.*, a prosthetic group and a high-molecular carrier. Symplexes are distinguished from mere mixtures by one or more of the following characteristics: (1) alteration or enhancement of the specific reactivity of one component; (2) change in solubility or dispersion of one component; (3) change in optical properties; (4) change in stability; (5) change in toxicity; (6) change in reactions, *e.g.*, color reactions.¶

### *Inorganic Catalysts*

Let us now consider some of the aspects of *inorganic* catalysts which, because of their greater stability against heat, radiation,

\* Bredig, G. *Biochem. Zeit.*, 250, 414. 1932.

† Kuhn, R. *Resumé in Chemistry and Industry*, 1933, 52, 985.

‡ About 17,000 eggs (50 kilos dried egg albumen) yielded 50 mg. ovoflavine; 3,000 liters of cows' milk gave 60 mg. lactoflavine.

§ Willstätter and Rhodewald, *Z. physiol. Chem.*, 1934, 225, 103-24.

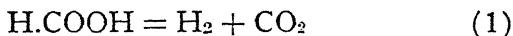
¶ Alexander, J. *Science*, 1934, 80, 79; 1935, 81, 44.

"poisoning," etc., have been amenable to a wider range of experimental procedure than have biocatalysts.

It is well known that the action of inorganic catalysts is not inflexible or invariable, but that changes of temperature, concentration, pressure, and "impurities" may greatly modify not only the quantities and the proportions of the products produced, but also the chemical nature of the products themselves. For example, under certain conditions of temperature, pressure, relative proportions, etc., a catalyst composed of equimolecular proportions of chromium and manganese oxides gave a yield of 80.5% methanol from a mixture of hydrogen and carbon monoxide gases, the gross reaction equation being  $2\text{H}_2 + \text{CO} = \text{CH}_3\text{OH}$ . On adding alkali metals to the catalyst, the nature of the output, under the same experimental conditions, varied greatly, and new or subsidiary compounds appeared in large amounts. Thus, with 9.8% rubidium in the catalyst, the compounds formed which were more complicated than methanol jumped from 13% to 46%, and these included many unusual alcohols and aldehydes.\*

The fact that a relationship exists between the activity and the arrangement of the metal catalyst atoms in the crystals of pure single metal catalysts (Fe, Ni, Co, Cu) and their mixtures, appears from the experiments of J. H. Long and others.† The reaction studied was the hydrogenation of benzene to cyclohexane, and the catalysts were subjected to X-ray diffraction examination, a procedure destructive to most, if not to all biocatalysts. The results indicate that preparations having exclusively a body-centered cubic lattice structure are inactive, while those having at least in part a face-centered cubic lattice are active.

To indicate how different catalysts may profoundly vary the course of chemical change, we may summarize some of the facts regarding the catalytic decomposition of formic acid, a comparatively simple compound:

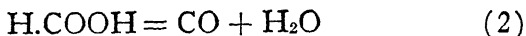


This form of breakdown is catalyzed at various rates and temperatures by Pd, Pt, Cu, Ni, Cd, and the oxides of Zn and Sn.

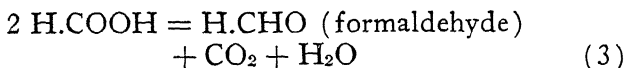
\* Morgan, G. T., D. V. N. Hardy, and R. A. Procter. Methanol Condensation as Modified by Alkalised Catalysts, *J. Soc. Chem. Ind.*, 52, 1 T. 1932.

† Long, J. H., J. C. W. Frazer, and Emil Ott, *J. Am. Chem. Soc.*, 54, 1101. 1934.

Pd and Pt sponges bring total decomposition at 245° and 215° respectively:



This change is catalyzed by  $\text{TiO}_2$  and blue oxide of tungsten.



This change is catalyzed by  $\text{SiO}_2$ ,  $\text{ZrO}$ , and uranous oxide.

Thoria may produce changes (1), (2), and (3), depending on temperature.

Large-scale chemical industries depend upon the use of catalysts; *e.g.*, the hydrogenation of soft fats, to harden them; the manufacture of phthalic anhydride and of maleic acid. Most concentrated sulphuric acid is now made by vanadium oxide or platinum catalysts, and the huge production of ammonia ( $\text{NH}_3$ ) from gaseous hydrogen and nitrogen, as well as the conversion of the ammonia into nitric acid and nitrates, essential both in agriculture and the explosive and other industries, is carried on by catalysts. The technological and patent literature indicates only partially the great extent to which industrial catalysts owe their efficiency to the presence of relative small, often minute percentages of "impurities" or additions, known as *promoters* because they facilitate a desired reaction. On the other hand, substances which coat over or combine more or less irreversibly with the catalyst, so that its activity is injured, are known as *catalyst poisons*. Where a catalyst is capable of conducting several different changes simultaneously and inhibitors are found which prevent the unwanted reactions, we speak of *beneficial poisoning*.

### *Differentiation*

With plants and animals, we are faced with the astounding fact that from a single cell, the zygote, there arise a great variety of tissues, organs and structures, containing cells *differentiated* from the original zygote cell, and capable of highly specialized functions. What physico-chemical mechanism underlies these developments?

The zygote consists of self-reproducing units (genes, mitochondria) with a much larger mass of molecules and molecular groups which are incapable of self-duplication (the cytoplasm

with its solutes, enzymes and other colloidal particles; food deposits, such as starch in seeds, albumin and yolk in eggs). Evidently the emergence of a new kind of cell must involve a persisting change in any or all of the following: (1) the basic living catalysts; (2) the secondary, non-living catalysts of the cell; (3) the conditions under which the catalysts function.

The regular course of differentiation cannot be accounted for by assuming a fixed series of mutations or by chromosomal aberrations, for such variations are sporadic and no mechanism for an orderly sequence of them is evident, or even conceivable. The view at present most generally accepted is *variation in balance of genic function*, which is stated by Prof. T. H. Morgan in his Nobel prize address \* as follows:

It is conceivable that different batteries of genes come into action one after the other, as the embryo passes through its stages of development. This sequence might be assumed to be an automatic property of the chain of genes. Such an assumption would, without proof, beg the whole question of embryonic development, and could not be regarded as a satisfactory solution. But it might be that in different regions of the egg there is a reaction between the kind of protoplasm present and the specific genes in the nuclei; some genes being more affected in one region of the egg, other genes in other regions. Such a view might give also a purely formal hypothesis to account for the differentiation of the cells of the embryo. The initial steps would be given in the regional constitution of the egg.

The first responsive output of the genes would then be supposed to affect the protoplasm of the cells in which they lie. The changed protoplasm would now act reciprocally on the genes, bringing into activity additional or other batteries of genes. If true this would give a pleasing picture of the developmental process. A variation of this view would be to assume that the product of one set of genes is gradually in time overtaken and nullified or changed by the slower development of the output of other genes, as Goldschmidt, for example, has postulated for sex-genes. In the last case the theory is dealing with the development of hybrid embryos whose sex-genes are assumed to have different rates of activity.

\* Morgan, T. H. *Scientific Monthly*, July, 1935.

A third view may also be permissible. Instead of all the genes acting in the same way all the time or instead of certain kinds of genes coming successively into action, we might postulate that the kind of activity of all the genes is changed in response to the kind of protoplasm in which they lie. This interpretation may seem less forced than the others, and in better accord with the functional activity of the adult organism.

This last-mentioned view somewhat resembles the theory of catalyst modification described later on; but in the latter, genes and/or enzymes are supposed to be altered in their action, by specific substances in the cytoplasm of the zygote or formed earlier in the course of development.

Prof. Richard Goldschmidt outlines two general notions underlying individual developmental processes "so carefully interwoven and arranged, so orderly in time and space that the typical result is only possible if the whole process of development is, in any single case, set in motion and carried out upon the same material basis, the same substratum and under the same control by the germ plasm or the genes." \*

The first notion is that "the action of the genes in controlling development is to be understood as working through the control of reactions of definite velocities, properly in tune with each other and thus guaranteeing the same event always to occur at the same time and at the same place. . . ."

The second notion, developed from experiments in embryology, stresses the interrelation of two types of differentiation: (1) *Independent differentiation*, wherein "a once-started process of differentiation takes place within an organ or part of the embryo, even if completely isolated from the rest." (2) *Dependent differentiation*, which "requires the presence and influence of other parts of the embryo for orderly differentiation."

For example, if in a vertebrate embryo the *group* or clone of cells constituting the primordium (or precursor) of an optic cup be transplanted, at a suitable stage, to a new location, it will nevertheless develop into an eye with its lens. But if that portion of the skin of the head which is to form the lens of the eye is transplanted, no lens is formed because the presence of the clone of eye cells is necessary for the determination of a lens.

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\* Goldschmidt, R. *Science*, 78, 539-47, 1933.

Again, if young pupae of the Central-European, swallow-tail butterfly are treated with extremely low temperatures, some of the individuals hatched cannot be distinguished from typical Palestinian subspecies. The characteristic features are *heritable* only in the case of the Palestinian form.

An explanation is very simple on the basis of the assumption that in the developmental processes in question reaction-velocities are involved; the external influences in question change the rate of some reaction or system of reactions underlying the differentiation of the character in question, and the mutation which produces the same phenotypic effect is a change in a gene, which controls the same differentiating reaction, with the effect of a corresponding change of speed of the reaction.\*

Goldschmidt further states: "The most probable mutational change with a chance to lead to a normal organism, is a change in the typical rate of certain developmental processes." As has already been shown, modification of a catalyst may change the rate and/or the *nature* of catalytic reactions. But Goldschmidt suggests no mechanism whereby the reaction velocities can be so delicately balanced by the *unchanged* genes of the zygote that they can determine the complex and orderly development of an individual, and especially the profound differences in cell clones incident to differentiation. Changes in temperature and other variable external factors always exert their effect, as one may read in the annual rings of trees, which constitute a record of past weather conditions. But *something more certain than the vagaries of the general milieu* must be invoked to explain the orderly course of life in the face of ever-changing external conditions.

### *Catalyst Modification*

The view has been advanced † that genes and enzymes are capable of undergoing *modification*, a more or less lasting alteration in the catalysts themselves resulting from the *fixation* (by adsorption or by chemical combination) of *definite substances* (ions, atoms, molecules or other particles), as a result of which the *nature* as well as the rate of catalytically directed changes may

\* Goldschmidt, R. *Science*, 78, 539-47, 1933.

† Alexander, J. Some Intracellular Aspects of Life and Disease, *Protoplasma*, 14, 296-306. 1931. *Scientia*, October, 1933. *Archivio di Sci. Biol.*, 14, 409-13. 1934.



be profoundly altered *along definite lines* according to the modifiers present, despite uniformity of, or even in the face of great variations in, gross milieu conditions. Within limits, the ship of life holds to its course in defiance of wind and wave. Plants and animals tend to develop true as well as to breed true.

The source of the modifying particles in the case of normal development is twofold: (1) specific molecules in the cytoplasm of the zygote or its incidental surrounding structures; (2) new specific molecules produced catalytically as development proceeds. The quantities necessary to produce directional changes are extremely minute—in theory, one molecule can modify one gene or enzyme particle. Immunologically, sensitization may be produced by as little as 0.000,05 mg. of specific protein, and for years thereafter an immunized animal can produce highly specific anti-body. If the animal is bled, a further supply of anti-body develops. Less than 0.000,000,000,1 mg. of many substances per liter (vanillin, ionone, artificial musk) can be detected by smell; but this tiny amount represents, with vanillin about 40,000,000 molecules, only a few of which actually reach the cell to produce the changes we recognize as an odor or "smell." It does not seem unreasonable to think that the effect of the odorous substance is, in some cases at least, due to its effect on cell catalysts.

Modification is, then, *chemical determinism*, not through the reactants but through the biocatalysts which direct the devious courses of reaction and chemical change. Modification is based not on changes in the highly variable molecular grist passing through the mill, but rather on changes in the effectiveness of the mill itself through alteration of its grinding and cutting jaws. Modification is, therefore, analogous to the employment of catalyst promoters in chemical technology, except that biocatalysts are very easily altered. Consider the cytological evidence in crossing-over, inversion, translocation and deletion, and it is evident that the gene-string must be of a rather soft, sticky nature, quite different from the hard metallic or inorganic catalysts; so that fixation of modifying particles by biocatalysts should be relatively easy.

Prof. Richard Willstätter and his pupils \* have done valuable work in the closely related field of *adsorption* of enzymes by

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\* R. Willstätter, in Alexander's "Colloid Chemistry," Vol. II, pp. 361-6, (1928).

various substances (e.g., aluminum hydroxide, ferric hydroxide, stannic hydroxide, kaolin, silicic acid, calcium phosphate, cholesterol, tristearin, etc.), and the subsequent *elution*, desorption or release by various methods (e.g., change of solvent, of pH of the milieu, of chemical structure of the adsorbent as when tricalcium phosphate is converted into dicalcium phosphate). He produced enzymes in high concentration: invertin 2,000 times more concentrated than in the fresh yeast used; peroxidase 12,000 times more concentrated than in the dried plant root; lipase 300 times more concentrated than in the desiccated and de-fatted liver. We see here an indication of how milieu and adsorbent changes may direct the fixation, as well as the release or elution of modifiers for genes and for enzymes.

### *The Course of Differentiation*

Certain physical conditions naturally develop as growth proceeds. With many animals, the typical development of the zygote leads first to the formation, by progressive cell division, of the "mulberry-mass" of cells which used to be called the *morula*, a term now restricted to one type of blastulae lacking an interior hollow or blastocoele. (A. Richards, "Outline of Embryology," p. 94. J. Wiley & Sons, 1931).

Since living cells show internal motion and since chemical reactions within the cells must develop at least a slight thermal gradient, convection must play some rôle in the chemical and physical interchanges involved in growth. But diffusion is the main process whereby gases, solutes and ions are interchanged between the developing *zygote* and the milieu. When the *morula* is of sufficient size, a *diffusion gradient* must come into evidence, and the consequence of *differential diffusion* become manifest.\* Some ions and molecules diffuse more rapidly than do others, resulting in the establishment of zones of variation in ionic and molecular concentration; and besides these qualitative and quantitative differences, the *time factor* in diffusion becomes increasingly important. With a single cell, in contact on all sides with the milieu, diffusion is both rapid and equalized. With the much larger *morula*, it is obvious that the interior cells must draw

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\* Alexander, J. Selective Absorption and Differential Diffusion, *J. Am. Chem. Soc.*, 39, 84-8. 1917. The ultramicroscope shows intense particulate activity within the cell, which may be in part due to diffusion at catalyst surfaces.

upon the resources of the milieu more slowly as well as to a degree different in nature as well as in amount. The same considerations apply to the removal into the milieu of what are termed the "waste products" of metabolism. As Prof. A. Krogh \* has shown, "the diffusion constant for  $\text{CO}_2$  in tissues is some thirty times higher than for oxygen."

The question as to why the cells of the morula tend to cohere is answered, in principle at least, by the work of C. Herbst, who found that while all of the salts of sea-water are important for the development of echinid eggs, in the absence of calcium salts the cells of the embryos would fall apart but would nevertheless live and develop further.† Calcium plays an analogous rôle in soils, where the presence of calcium "humate" is necessary for the aggregation of soil particles consonant with what agriculturists call good tilth. Alkali soils are pasty and sticky, and tend to wash away.

Because of their location relative to the food supply, cells on the outside of the morula grow and duplicate at a more rapid rate than interior cells. This demands an increase in external surface, which is possible only in one of two ways: (1) formation of a *diverticulum* or projection of the "skin"; (2) *invagination*, a bending inward of the surface to form a pocket or sheath. Since the "skin" cells cohere strongly to those within, only invagination can occur, and there results the well-known two-layered *gastrula*.

Quite diverse embryological structures are found in various animals. In what has been stated above, only solid blastulae (morulae) have been considered. But it is quite evident that analogous considerations apply to the various other embryological types. Thus Richards points out (*lib. cit.* p. 99) that in single

\* A. Krogh, *The Anatomy and Physiology of Capillaries*, 1st ed. 1922, p. 201.

† Following the first mitotic division of a developing zygote, it sometimes happens that the two cells separate, each cell going on to develop into a separate individual. Twins of this origin are known as *identical twins*, because as a consequence of their having precisely the same genic structure they are almost exactly alike (same sex, same placenta, appearance and characteristics, even like finger-prints). Ordinary ("fraternal") twins, arising from the fertilization of separate ova, may differ greatly, and are often of different sex. Among insects, development of individuals may not occur until after many splits in the original zygote, so that one egg may give rise to many individuals. This is called *polyembryony*, and was discussed by Dr. Filippo Silvestri at the Harvard Tercentenary (1936). The Dionne quintuplets look as though they had developed from the same original zygote (see Kirkpatrick and Hüttner, "Fundamentals of Health," 2nd ed., Ginn & Co., 1937). Each pair of eighteen sets of identical twins gave the same brain electrograms (Drs. Hallowell Davis and Pauline A. Davis, *Science Supplement*, 1936, 83, 12).

layered blastulae of certain kinds invagination is evidently due, mainly at least, to lateral pressure exerted on the endodermal plate by the excess rate of growth of cells in the "vegetative" pole over the rate of growth of cells in the ectodermal section. Here there has evidently already occurred a differentiation of cells, understandable on the basis of a segregation of modifiers. Thus a hollow rubber ball immersed in gasoline will immediately absorb this rubber solvent superficially and will seek to increase its surface, invagination tending to occur at the weakest area.

The formation of the gastrula enforces a new set of conditions, for the gastrula cavity constitutes a sort of "bay" or inlet from the "ocean" of the milieu; and this "bay" will have, or promptly develop, molecular and ionic concentrations different from those of the exterior "ocean." Cells facing the "bay," through originally "skin" cells, may be expected to undergo change in response to their new environment, *with a shift in the adsorption and elution of catalyst modifiers*, as well as in the position of the cells relative to diffusion. Thus there tend to emerge *three typical environmental zones*, corresponding to the *ectoderm, mesoderm, and endoderm*. Just what will happen in these zones as a result of catalyst modification changes enforced by ionic or concentration changes, or because of alteration in the conditions for catalysis, will vary from case to case, as the catalysts and modifiers vary. There is no necessity of assuming or expecting that the same definite mesodermic and allied layers must develop in each embryo. Though differentiation becomes marked after gastrula formation, further growth and development may differ widely in different kinds of animals.

Without pursuing the embryological picture further, we may quote some remarks of Prof. H. S. Jennings (Johns Hopkins University)\* on differentiation, which he terms "one of the darkest questions in biology" (p. 234):

Every cell contains as a rule all the genes, and so far as genes are concerned could produce an entire individual. But after a while, through the continued activity of the genes, many different substances have been manufactured from the cytoplasm, and are located in the different cells. Things have now changed so much, and have become so fixed, that the genes can no longer start anew from the

\* Jennings, H. S. "Genetics," New York, 1935.

beginning. At a much later stage therefore a single separated cell will no longer produce an entire organism, or any required part of the organism, although it still contains all the genes. With age cells become fixed in their ways, as old individuals do.

But this condition in which any cell can produce any one of many different parts of the body, depending on circumstances, may continue into a rather late period of development, particularly in vertebrates. At a certain time the egg of such a creature as a frog has become a mass of small cells. Under normal conditions, when we examine this mass, we can predict what part of the adult each part will produce. Cells here will produce the brain, there at the sides the eyes, here the ear, there the spinal cord, here parts of the skin. If we leave the egg to itself, these are indeed the parts that will be produced.

But this is not because each cell can produce only that part and nothing else. . . . What happens is that from a certain spot on the egg—a recognizable spot—an organizing influence starts out, so that this spot is known as the organizer, or the organization center. This organizing influence, whatever its nature, creeps from cell to cell, causing each cell to alter internally—through the interaction of its genes and cytoplasm—in such a way as to produce the structures of the embryo. Each cell that is reached later transforms in such a way as to fit the cells that have gone before—in such a way as to make the next proper part in the pattern of the body.

Speaking of the effects of hormones (thyroid, hypophysis, etc.), Prof. Jennings states\* (p. 237): "The genes first act to produce different chemicals. Then these diverse chemicals cause the cells to develop in certain particular ways, so as to give rise to diverse parts." And later (p. 240) he refers to the fact that by treatment with thyroid extract the aquatic Axolotl (which can live, reproduce and die as such), becomes transformed into its land-living form, Amblystoma, and that this transformation will also take place when the Axolotl is forced out of the water, *e.g.*, as when streams dry up. "There is little doubt that what these conditions do is to cause the thyroid of the animal to discharge its secretion into the blood, and this induces the transformation."

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\* Jennings, H. S. "Genetics," New York, 1935.

Chemical embryologists have been attacking the problem of the chemical nature of the "organizer." Needham and his co-workers \* are on the track of one of these important and elusive substances, but it does not seem that the tiny amounts of specific molecules will soon be separated and identified. However, another form of approach to the problem is open, namely, observing the effects of substances of known composition upon living units. Isolation and identification of the various vitamins and hormones, coincidentally with observations of their effects, is work along this line. Vitamins may be considered in the light of hormones produced extra-corporally, for both are effective in extremely small amounts.

### *Disease as Due to Abnormal Modifiers—Cancer*

If many of the normal procedures of life are due to *normal* modifiers of biocatalysts (genes and enzymes) we must expect that the presence of *abnormal* modifiers will in many cases at least, produce abnormal procedures and conditions which if sufficiently marked will constitute disease. There are, of course, many other "causes" of disease, but frequently on tracing back through the casual sequence, we find some substance or some definite chemical compound which influences the cells to act abnormally. It is this intracellular aspect which will be briefly considered, taking *cancer* as an example.

In the absence of etiological knowledge, cancer was described on a pathological basis as a growth of cells of the body, which is progressive and invades healthy tissue. About ten years ago, genetic considerations led me to believe that if a body cell underwent a mutation which would result in abnormally rapid increase, such a rapidly growing cell clone, without adequate vascular supply, could present any or all of the clinical aspects of cancer—tumor, ulcerative breakdown, metastases, etc. In 1902, Boveri † suggested that cancer might be due to genetic factors. The writer more recently ‡ stated:

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\* Needham, J., C. H. Waddington, and D. M. Needham. Physicochemical Experiments on the Amphibian Organizer, *Proc. Roy. Soc. Lond.*, B114, 393-422. 1934. Prof. Hans Spemann (Univ. of Freiburg) received the Nobel prize for his work in this field.

† Boveri. Zur Frage der Entstehung Maligner Tumoren, Jena. 1914.

‡ Alexander, J. Colloid Chemistry, Theoretical and Applied, 3rd Edition, D. Van Nostrand Co. 1929.

The cancer cell may be considered as a type of evil mutant, which, being formed or activated in a larger organism, duplicates itself within its host, with destructive consequences. This view harmonizes with the fact there are several kinds of cancers, as well as the evidence that a cancer-mutant may be produced or activated by several different types of proximate causes, especially those which produce gene-mutation—X-rays, heat, and chemical substances (certain tars). Since cancer cells reproduce true to type, even when transplanted, genic changes are evidently involved.

In the article in *Protoplasma*,\* the following was stated:

By *formation* of a cancer-mutant we understand that one or more of the genes in a normal cell undergo a mutation transmissible on cleavage. *Activation* of a cancer-mutant may be understood from the following considerations: Suppose that somewhere along the line of descent of the organism there had occurred a mutation in a gamete, leading to the transmission of an hereditary tendency toward gene-modification. The descendants of this parent would not inherit the modification, but might inherit a tendency toward modification, which would come into evidence *only if and when the modifying particles were present*. Thus persons with an inherited tendency to rag-weed hay fever would not even know it, if they were born and lived in countries free of rag-weed and its pollen. It is conceivable that an ultrafilterable virus or even specific molecules may cause modification in receptive genes; and if the modified genes would catalyze the formation of the modifying substance, continuous development of modified cells would ensue. In cases where normal organisms seem to be susceptible (*e.g.*, as in tar cancers), it is not even necessary to assume the existence of an inherited abnormal tendency to modification.†

Certain considerations involving the influence of specific chemical substances in cancerous conditions emerge from the experimental work in a number of fields, and should be considered in the light of catalyst modification, outlined above. It had long

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\* Alexander, J. Some Intracellular Aspects of Life and Disease, *Protoplasma*, 14, 296-306. 1931.

† It is now known that certain strains of mice resist implanted cancers, which others accept.

been known that cancer could be produced by application of certain tars (Yamagiwa and Ichikawa, *Mitteil. med. Fakultät., kaiser. Univ. Tokyo*, 1915, 15, 295), and in 1924-5 E. L. Kennaway and his associates (Research Inst. Cancer Hospital, London), finding that carcinogenetic tars could be obtained from a number of organic compounds by pyrolytic methods, began an intensive search for the cancer-producing substance in tar. It was finally identified as 1, 2-benzpyrene, a hitherto unknown hydrocarbon, present to the extent of about 0.003% ; and it was synthesized by J. W. Cook, Hewett, and Hieger (*J. Chem. Soc.*, 1933, 395). Prof. L. F. Fieser (Harvard University) has reviewed the astounding analytic and synthetic work of the organic chemists of many countries \* which has served to show that many resin acids, alkaloids, sterols and bile acids, saponins, heart and toad poisons, sex hormones and carcinogenetic substances are all, in one way or other, to be considered as derivatives of phenanthrene. (See "The Chemistry of Natural Products Related to Phenanthrene," by L. F. Fieser; *A. C. S. Monograph No. 70*, Reinhold Pub. Co., 1936.) While in its isomer, anthracene, the three benzene rings are in straight-line formation, one of the rings in phenanthrene is offset. This slight difference in configuration makes a tremendous difference in the physiological significance of the compounds which develop when various rings, groups and side-chains are added to the three benzene rings which constitute both the anthracene and the phenanthrene nuclei.

Synthetic 1, 2-benzpyrene is just as potent as that isolated from tar—epitheliomas follow application to the skin, but connective tissue cancer (sarcoma) follows subcutaneous injection, and the induced tumors resemble those which arise spontaneously. Then a still more potent cancer-producing substance, methylcholanthrene, became the focus of investigations, many of them by Prof. Fieser and his collaborators, who obtained it from cholic acid found in bile. "While proof is entirely lacking, it appears possible that many forms of cancer may originate in the metabolic production of methylcholanthrene or related substances from the

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\* Because of the minute quantities of material available for the investigation of cholic acid, Pregl was led to develop his now classical methods of chemical analysis, for which he was awarded the Nobel prize. Among the many other workers in this field, Windaus and Wieland have also received the Nobel prize.



bile acids, or perhaps from the sterols or sex hormones, of the body."

Since growth of a transplanted tumor is more rapid than one originally produced by this hydrocarbon, some permanent change in the cell catalysts (genes or enzymes) appears to be involved. Pure, inbred strains of mice are highly susceptible to implantation of tumor tissue, and the "takes" are malignant. Prof. Fieser states that methylcholanthrene is the most potent carcinogenetic substance at present known.

Dr. F. S. Hammett and his associates (Research Inst. Lankenau Hospital, Philadelphia) believe that "The sulfhydryl-partially oxidized sulfhydryl groups comprise the chemical elements of a naturally occurring chemical equilibrium through which growth by increase in cell number is regulated" in vertebrates (Protoplasma, 1930, 11, 382). Injection of minute quantities of cystine disulfoxide into 91 mice with spontaneous tumors showed (as against 65 controls) both gross and microscopic ameliorations, indicating retardation of proliferation of the tumors. (Science, 1936, 83, 108-9.) See also editorial in Am. J. of Clin. Path., May, 1936, by Dr. Stanley P. Reimann of this group.

Cancers may also follow excessive smoking, exposure to certain kinds and dosages of X-rays, burns (*e.g.*, among natives of parts of India, who carry suspended from their waists a "fire-box" with hot coals). It seems likely that definite chemical compounds arising from pyrolysis, molecular rearrangement, or other chemical change, and *operating as catalyst modifiers*, underlie the phenomena of cancer. And since transplants can be carried on from animal to animal, it seems evident that the specific modifier or electronic pattern area must be continually reproduced and increased, so that more and more normal cells can be affected.

### *Immunity*

About 1909 with Dr. J. G. M. Bullowa I observed in the ultramicroscope that the toxins and antitoxins of diphtheria and of tetanus mutually coagulate each other,\* but one toxin will not

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\* Alexander, J. Selective Absorption and Differential Diffusion, *J. Am. Chem. Soc.*, 39, 84-8. 1917,

coagulate the other antitoxin. In the formation of anti-body, the toxin seems to become an essential part of the directive specific electronic surface of a catalyst particle or surface, which determines the formation of particles having an electronic surface contour *opposite* in form, and therefore capable of specific reaction or combination with new particles of the antigen when they appear.\* But some of the evidence mentioned above seems also to indicate that specific particles when attached into an enzyme complex (or "symplex") may mould out particles having the *same* electronic contour as themselves, *and thus duplicate themselves*. This seems to happen in the course of differentiation; for the number of specific molecules in the zygote does not seem capable for accounting for the modification of all modified cells in the adult body. A consideration of the possible causes underlying phenomena of this apparently contradictory nature (formation of like and of unlike electronic contours), may throw much light on what forces are operative in synapsis.

A piece of tin foil rubbed against the face of a coin acquires the *reverse* impression of the coin pattern on the side next to the coin; but on the exterior side the foil *duplicates* the coin pattern. Fixation of one face of such a duplex specifically moulded modifier, to a colloidal carrier, would leave the other *oppositely moulded face* exposed to the milieu.

### *Bacterial Dissociation*

It has for some time been known that many strains of bacteria are capable of existing in two forms, rough (*R*) and smooth (*S*), so termed from the appearance of their colonies. As a rule the smooth forms are more virulent than the rough. As an instance of the work in this field, the following is quoted from a paper by Dr. Eleanor G. Alexander-Jackson: †

It was found that a small optimal amount of ferric chloride, 0.0004%, representing  $2.5 \times 10^{-5}$  mols of iron per liter, added to Bordet-Gengou medium stimulated the dissociation of 2 human strains studied into completely smooth, convex, glistening colonies. These *S* colonies

\* Alexander, J. Some Intracellular Aspects of Life and Disease, *Protoplasma*, 14, 296-306. 1931.

† Alexander-Jackson, E. G. A Method for Obtaining Stable *S* Colonies of Human Tubercle Bacilli, *Proc. Soc. Exptl. Biol. Med.*, 31, 1101, 1934.

were produced in pure culture by one strain in the first generation, and by the other strain in the third generation on this medium. The fourth and fifth generations continued to produce *S* colonies.

Avian *R* bacilli were dissociated to *S* on modified Bordet-Gengou medium. The optimal amount of ferric chloride in this case was 0.004%, representing  $2.5 \times 10^{-4}$  mols of iron per liter. The lesions produced by the convex glistening colonies of both avian and human strains differed radically from those produced by the *R* bacilli. They were diffuse, inflammatory, and small or microscopic, whereas those produced by *R* bacilli were much fewer, limited, calcified, and larger. Virulence tests indicate that the *S* colonies of these strains possess somewhat greater virulence than the *R*.

### *Molecular Orientation as a Factor in Biological Phenomena*

Besides orientation, we have also to consider what Dr. Irving Langmuir terms (following Debye and Hückel) *deformation and segregation*.\*

Just what effect a molecule or particle will exert on a catalyst following its fixation by adsorption or otherwise, will depend upon *which part of the fixed particle is left exposed to the milieu*; and this, no doubt, will depend on the nature of the adsorbent. With "soft" particles like chromosomes and genes, changes in the milieu can register an effect.

Remembering that the gene-string (chromosome) is a *catalytically* active unit with a considerable cloak of "chromatin" through which diffusion is also taking place, we get some inkling of the forces at work within the close confines of the cell from the following remarks of Langmuir \* (*loc. cit.* p. 528):

Molecular deformation on close approach "is always such as to cause an attraction between the molecules."

In general, there will also be a tendency for molecules to be oriented when they approach one another sufficiently closely. This orientation always increases the attractive force.

\* Langmuir, I. "The Effects of Molecular Dissymmetry on Some Properties of Matter," in Alexander's *Colloid Chemistry*, Vol. I, 1926; also his subsequent papers.

Debye has also pointed out that if, around a given ion in an electrolyte, there were no concentration of ions of opposite sign, there would be no resulting attraction between an ion and its neighbors. But since there is in fact around any ion an increased concentration of ions of opposite sign, there is a resulting attractive force which opposes the osmotic pressure of the ions, due to their thermal agitation. It is this effect which we have denoted by the term *Segregation*. It may occur not only with ions, but also with dipole molecules such as those of water. By the segregation of dipole molecules, and their orientation about a given molecule or ion, electric forces may be transmitted through larger distances than would otherwise be possible.

In the paper by Alexander and Bridges \* (p. 12) it is stated:

Since the activity of a catalyst is determined materially by its outwardly directed fields of force, a change in the catalyst surface, *e.g.*, by chemical attack from the outside or through re-orientation of the component atoms or atomic groups, will modify or even inhibit its activity. Polymerism, tautomerism, and liability are well known to chemists and physicists, as examples of molecular rearrangement within the molecular boundary. It is quite possible that the surface charge of certain catalysts may be due to what may be called *electroversion*, whereby, following change in the nature of the milieu or change in temperature, certain atoms or atomic groups previously at the interior of the catalyst particle, move to the exterior and change places with other atoms or atomic groups or rotate so as to expose different outwardly directed surfaces or forces.

How the nature of the milieu influences the behavior of enzymes may be seen by watching the action of pepsin on coagulated egg albumen under the ultramicroscope. When hydrochloric acid is introduced, the coagulated clumps of albumin break up and resume the active Brownian motion they had lost on introduction of the pepsin solution, and then melt away, the field becoming brighter following their dispersion.† Let us next consider some of the meager facts known about pH differences within the cell.

\* Alexander, J., and C. B. Bridges. "Some Physico-Chemical Aspects of Life, Mutation, and Evolution," in Vol. II of *Colloid Chemistry*. 1928 (Chemical Catalog Co.).

† Alexander, J. *J. Am. Chem. Soc.*, 32, 680, 1910.

*pH Differences Within the Cell*

According to Prof. Robert Chambers\* the nucleus of the normal immature starfish egg is feebly alkaline, showing a pH of 7.6—7.8, whereas the cytoplasm is feebly acid at pH 6.6—6.8. When injured, the cytoplasm becomes more acid, pH 5.4—5.6.

These differences seem small, but we must recall that the pH figure is of logarithmic nature, exerting an *exponential* effect on the figure expressing the physical fact—the concentration of hydrogen ions (see p. 30).

SOME PHYSICO-CHEMICAL ASPECTS OF LIFE, MUTATION  
AND EVOLUTION †

One of the commonest, most interesting, and yet most inscrutable of natural phenomena is the transfiguration of non-living matter into living matter by growth or reproduction, and the reverse transformation of the living into the non-living by decline and death. The material mechanism of life and of death is understandable in terms of well known and readily comprehensible physico-chemical concepts. The chemist and the physicist, starting with atoms and electrons, have been working upward into larger and still larger molecules and molecular groups, while biologists have been steadily working downward to smaller and still smaller cellular units. Putting it figuratively, these two groups of scientists have been tunnelling into the mountain of ignorance from opposite directions; they have met in the median zone of colloidal dispersion, and the two bores seem to justify or register perfectly.

Many of the difficulties which confront those who seek to understand the nature of life and life processes, arise from the fact that attention has not been focussed upon vital units sufficiently simple in their nature to be sufficiently comprehended in both structure and behavior. Even the smallest cell or monocellular being is an exceedingly complicated structure composed of many millions of molecules. It presents within its confines and purview whole series of simultaneous and interrelated phe-

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\* Chambers, R. "The Nature of the Living Cell as Revealed by Micro-manipulation" in *Colloid Chemistry*, Vol. II, pp. 467-468.

† Based on a paper by J. Alexander and Calvin B. Bridges in Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied."

nomena. We are mentally incapable of envisaging the whole *mélée* at once. If we would form a precise mechanical picture of what occurs in life, we must dissect down through the layered structure of matter, until we reach the simplest unit which can be regarded as living. As the complications of structure fall away, the tiny ultimate vital units indicate that, from their ultra-microscopic domain, they direct and dominate the material changes of life. The genetic evidence (especially linkage and crossing-over) indicates that each gene (the chromosomal sub-unit), actually reproduces itself *next* to itself. Normally, genic reproduction is self-duplication *in situ*.

Since the addition, removal, or alteration of these sub-units produces marked and characteristic changes in the cell and in what develops from it, we are justified in regarding them as specific catalytic particles which direct chemical changes within their respective domains, and thus dominate life processes, subject, however, to modification by specific molecules, inherited in the parental cytoplasm, acquired in the nourishment, or formed within the developing organism. It is the genes within the gene-strings or chromosomes, and probably also the cytoplasmic modifiers, which determine whether a certain cell will develop into a flea, an elephant, or a man.

To epitomize the biological evidence, we have colloidal particles of the order of molecular dimensions, which actually duplicate themselves from what is admittedly non-living matter, and which control and direct the material changes of life. How can we explain such behavior in the light of our present chemical and physical knowledge?

Having in mind the highly specific nature of complex catalysts (see p. 369), let us imagine a simple molecule approaching and fixing itself at the surface of a particle having appropriate opposite charges to those which the simple molecule presents.

As soon as the oppositely charged areas come within their critical range, their mutual neutralization must cause a reshuffling of all the electronic fields involved, so that the molecule after its fixation will present to the milieu a different configuration from what it presented before fixation. It might now be able, on its own account, to make other attachments previously not possible. The attachment of a second molecule to the first would once more cause a reshuffling of all the electronic fields involved. Now if

the bond between the two molecules were to hold, while the bond holding them to the fixation particle were to break, we would have released to the milieu a new duplex molecule, while the fixation surface would be free for renewed action. The subjoined figure (Fig. 38) shows diagrammatically a synthetic catalysis of

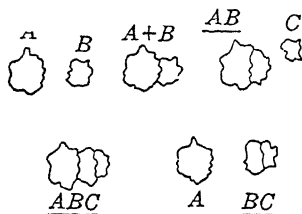


Fig. 38. Diagrammatic representation of synthetic catalysis.

this character. It is evident that a reversal of the process would represent an analytic or destructive catalysis.

This is the most general statement of the process. In particular cases the union of catalyst and substrate may be a transient or unstable chemical compound.

Suppose now that we have a catalyst particle composed of several simple molecular sub-units, which is on one of its areas

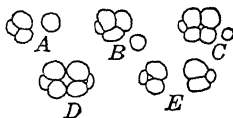


Fig. 39. Diagrammatic representation of a single type of reproductive catalysis (or autocatalysis).

conducting a continuous catalysis like those just described. Suppose that at some one of its other areas the catalyst fixes or adsorbs successively the several sub-units of which it is composed; that because of the order of their fixation or because of subsequent inter- or intramolecular changes, these component sub-units form a group identical with the fixation or catalyst group; and suppose lastly that the duplicate particles now separate or are separated, *e.g.*, by elution. (See Fig. 39.) Each would be an exact duplicate of the other in catalytic and in self-duplicating behavior, and our original particle could be properly called an

*autocatalytic catalyst*. It would duplicate itself from non-living matter and also would direct and control chemical change; and in these respects as well as in size, it would be identical in the nature of its behavior, with the simple genes we have essayed to explain. It would have to be considered as *living*.

The question naturally arises: Is there in nature, apart from the genes in a gene-string or chromosome, anything resembling our hypothetical free-living, self-reproducing catalyst particle? We believe that in the bacteriophages and the so-called ultrafiltrable viruses we are dealing with living beings (bionts) approaching or actually of this degree of simplicity. It is quite possible, though as yet unproven, that in some cases these ultimate biological units may be molecules, even if large ones. (Since this was written, Stanley has crystallized the tobacco mosaic virus.)

To those who have brought the experimental proof, it is no longer news that if, prior to the self-duplication of a gene, the gene itself is modified by some non-lethal agent (X-rays, heat, chemical substances or variations in the milieu) the gene or genes thus affected may reproduce steadily true to the modified form; and the cell containing such modified chromosomal material, as well as the living being (biont) formed from it, will show or tend to show the consequences due to the changes in the nature and action of its controlling catalysts, the genes. (See p. 325.) Thus arise mutations, and thus proceeds evolution; for apart from symbiotic cellular inclusions like chloroplasts, inheritance is carried mainly by the genes in the chromosomes. Strains whose mutations are not disadvantageous or lethal, will survive; if the mutations are advantageous, the strain will tend to dominate.

Considering now the bearing of these ideas on the origin of life, the law of probabilities makes it evident that no biont as complicated as even an amoeba or a bacterium could have arisen spontaneously, without precursors. Much more likely is it that the first living thing was a molecule or simple molecular group exhibiting the directive and self-duplicating power shown by genes. Indeed, in this ultramicroscopic zone, spontaneous generation may be continually occurring, without being recognized. The fact that no one has yet produced an autocatalytic catalyst does not mar the demonstration of their existence. We can no



more deny the existence of the genes of a giraffe than we can deny the existence of the giraffe itself.

Diagram (Fig. 40) wherein time is indicated logarithmically, as well as the other figures, are taken from Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied." It indicates the biological and evolutionary relations above referred to.

### THE PHYSICO-CHEMICAL MECHANISM OF EVOLUTION

The cell from which an individual develops (the zygote) must contain such catalysts or catalyst modifiers as will determine

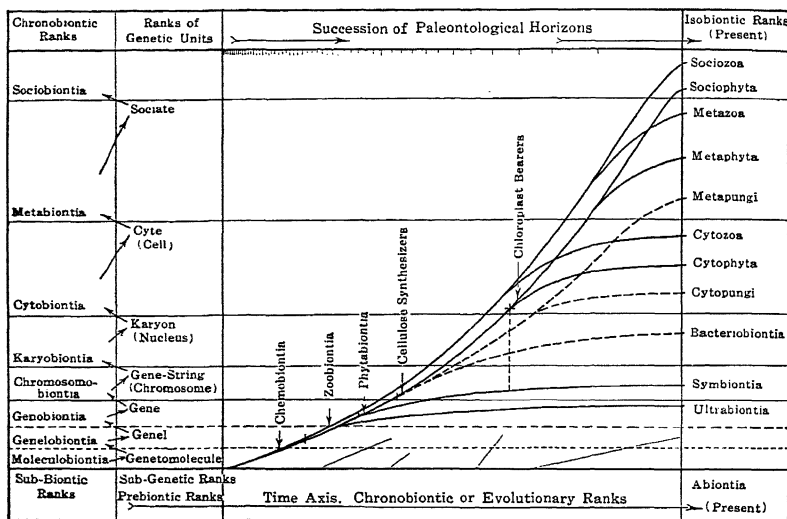


Fig. 40. Diagram of ranks of living units.

the formation of the substance and structure of that individual under suitable milieu and food conditions. If a zygote develops abnormally under normal conditions, we may assume that there has been an alteration in the *quantity*, the *ratio*, or the *nature* of either (1) its gene-plasm, or (2) its catalyst modifiers. *Gene-plasm changes* may be effected by mutations (which alter quality) or by chromosomal aberrations (*e.g.*, deletion, polyploidy, etc., which alter effectiveness and quantity). If transmissible to descendants, gene-plasm changes may determine changes in the

plant or animal which would be recognized as steps in evolution.\* (See Section on Genetics.)

If *heritable changes* were to arise in the *cytoplasmic catalyst modifiers* deposited in the zygote, we would here have another mechanism whereby evolutionary changes could be effected. Proof of such a mechanism remains to be established. The potency of such cytoplasmic inclusions in the zygote is evident when we consider the "organizator" of Prof. Hans Spemann (Univ. of Freiburg, Nobel Laureate) and the "evoker" of Dr. Joseph Needham (Cambridge University).

Let us first consider how such modifiers (catalysts of the catalysts) might reach the sex cells (gametes) which unite to make the zygote. They may be formed within the gamete, or reach it from the outside through the agencies of the circulation and diffusion. In the latter case, they may be formed in somatic cells or they may enter the circulation from food via the digestive tract.† The larger the number of modifier molecules formed within or introduced into the body of a parent, the greater the probability of their entering into and remaining within the parental gamete. Hypertrophy or atrophy of a part or organ, which sometimes follow excessive use or disuse, might thus effect the *quantity* of specific circulatory substances originating in such part or organ. New molecular individuals, entering the organism through food, might reach the gametes directly, or through their effects in other cells. Furthermore, changes in environment, apart from food, might register their effects through variations in quantity, ratio, and nature of modifiers produced within the organism.‡

In considering some chemical aspects of life, food, and evolution, J. Alexander (Scientia, Oct., 1933) pointed out that we are,

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\* Dr. Karl Landsteiner (Rockefeller Inst. for Medical Research, Nobel Laureate) begins his recent book "The Specificity of Serological Reactions" (1936) with the following words: "The morphological characteristics of plant and animal species form the chief subject of the descriptive natural sciences and are the criteria for their classification. But not until recently has it been recognized that in living organisms, as in the realm of crystals, chemical differences parallel the variation in structure."

† Substances entering the circulation from the digestive tract may produce urticaria (hives) and similar "food allergy" effects in sensitive individuals.

‡ In this connection see "Hormones and Heredity" by J. T. Cunningham (Macmillan Co., 1921), reviewed by M. F. Guyer in J. of Heredity, 1923, 14, 136-8.

chemically, heavily in debt to other living beings (bionts) for the chemical molecules essential to our life and development, be their minimal amount relatively large, or small, or even minute as with vitamins. Such substances as we produce with our own catalysts, start mainly with what other life gives us.\* In general, the higher the form of life, the more dependent it is upon simpler forms to supply it with the essential specific molecules, which the analytic and synthetic action of its catalysts moulds into its own species-specificity. The riddles presented by the disappearance of various plant and animal species are, naturally, open to many possible interpretations, *e.g.*, changes in climate, pestilence, extermination by the competition of other species. A more subtle but equally potent possibility is food failure—not necessarily actual famine, but a deficiency in the supply of certain foods which furnish small quantities of essential substances, or else the failure of the plants or animals furnishing such substances to produce them in sufficient quantity. Such deficiencies may even result from a voluntary or a forced change of diet, as seems to be the case in pellagra and some forms of anemia. Foods may also cause incapacitating if not fatal disease, *e.g.*, lathryism, trembles, loco-weed disease, selenium poisoning.

Certain data may be read in the light of the hypothesis of heritable change or adaptation to a certain milieu, arising from changes in cytoplasmic molecular make-up. Paleontologists point to the fragmentary though coherent evidence of progressive adaptation, and taxonomists find analogous evidence in existing forms (*échelle des êtres*). Prof. William K. Gregory (Columbia University) states (Biol. Rev., 1936, 11, 311-44) that "the changes in many typical organic designs of known history may all be expressed as the resultant of two cooperative principles of individual development and phylogenetic evolution: the first may most briefly be called *repetition*, the second *emphasis*. The principle of repetition has long been recognized in part under such names as 'repetitive acceleration' (Cope), 'metamerism' (Gegenbaur), 'merism' (Bateson), 'aristogenesis' (Osborn), while the principle of uneven development or emphasis has been called

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\* "Rien n'est la proie de la mort; tout est la proie de la vie" (nothing is the prey of death; everything is the prey of life)—so runs a French aphorism.

'differentiation' (Spencer), 'alloiometry' (Osborn), 'heterogony' (Pézar, J. S. Huxley) and so forth. . . . Now one and now the other of these processes may predominate, but both are constantly altering organic designs to a greater or less degree."

Sufficient paleontological data enables Gregory to distribute the anatomical characters of an individual under two main causal headings: (1) *Habitus*, expressed by present feeding habits, locomotion, reproduction, etc.; (2) *Heritage*, representing characters surviving from much earlier ages and gained in adjustment to earlier environments. "As an example, we may say of ichthyosaurs that their general habitus was fish-like but their heritage was distinctly reptilian. But part of the habitus of the remote ancestor becomes part of the heritage of the descendant; we therefore observe that habitus and heritage are correlative terms, like father, son, and grandson. Hence in analyzing the successive stages of evolution of organic designs, we may often usefully qualify the words habitus and heritage so as to indicate their source or relative age."

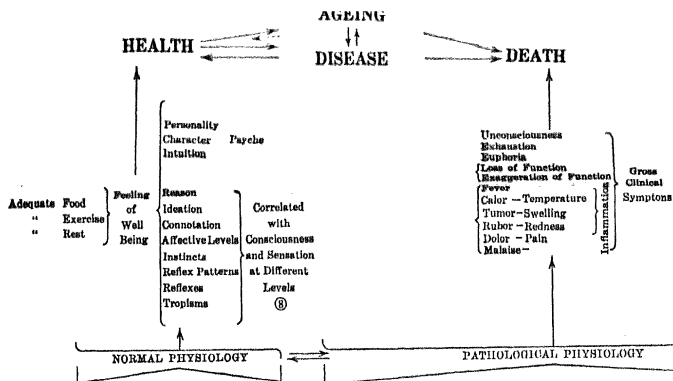
Among other items of interest in this connection are the results of N. H. Einhorn and L. G. Rowntree (*Science*, 1936, 83, 443; *Endocrinology*, 1936, 20, 342-7). They thymectomized four pairs of rats and found that although the growth and development of the operated animals did not differ materially from those of the unoperated members of the same litter, the offspring of the operated animals showed a progressive diminution of growth over four generations. Glutathione appears to be the main growth activating substance in the thymus gland (*Science Supplement*, Dec. 4, 1936, p. 9).

No matter how evolutionary changes are produced, natural selection will operate to favor those most suited to conditions existing at the moment. Native flora and fauna often suffer when brought into competition with strange plants or animals introduced *e.g.*, by geologic changes, or by man. Consider the rabbit and the prickly pear, which, when introduced, became pests in Australia, a continent that was for a long period more or less isolated.

To attempt to understand the chemistry of the catalytic action and of the autocatalysis of even the simplest ultramicro-

scopic biont, is in itself a formidable task. But when hundreds and thousands of genes join to form groups, chains or strings, where they and their products can mutually influence each other, the number of permutations and combinations becomes literally numberless. What happens is the result of a multitude of diverse factors and tendencies—*nature is, in fact, a compromise of tendencies.*





## STRUCTURAL AND FUNCTIONAL SYSTEMS OF THE HUMAN BODY

Order of Size	Level of Size	Support	Motion Oxidation	Control (Sensing) Nervous System Chemical Hormones	MAINTENANCE AND GROWTH ⑨ CIRCULATION REPAIR ELIMINATION						Reproduction	Protection	Stabilizations	
Visible Particles over 50 μ	Visible (Anatomy)	Bones Cartilages Bone Marrow	Muscles Tendons	Brain Plexes Nerves	SUPPLY	Lymphatic Lymph	Heart Arteries Veins Capillaries	Liver Gall Bladder Bile Gall	Kidneys Bladder Urine	Lungs Carbon Dioxide (CO <sub>2</sub> )	Skin Digestive Tract	Gonads Sex Organs	Reticulo- Endothelial System Spleen Antibodies Agglutinins Opsonins Complement Detoxification Phagocytes Spleen Liver	H-ion Concentration or Reaction (pH) Nerves Hormones Circulation Lungs Water Liver Kidneys Skin Tissue to Tissue Transfer Nervous System Temperature Skin Nerves Capillaries Evaporation Sweet (Salt) Oxidation - Reduction Potential (r) Immunity Active Passive Mineral Salt Balance
		③ Tissues	Tissues	Tissues	Tissues	Tissues	Tissues	Tissues	Tissues	Tissues	Tissues	Tissues	Tissues	
Microscopically Resolvable Particles over 100 m μ	Microscopic (Histology)	⑥ Cells Calcium Deposits Chromosomes	Cells Striated Smooth	Cells Neurons	Cells	Cells	Cells Leucocytes Erythrocytes Platelets Rouget Cells Controlling Capillaries	Cells	Cells Glomeruli Tubules	Cells Muscle Epithelia Ciliated	Cells Sweat Glands	Cells Ova Sperm		
		RESPIRATION FERMENT												
Colloidal Particles 2 - 100 m μ	Ultra- Microscopic (Colloid Chemistry)	Genes Enzymes Sols-Gels	SURFACE SPECIFICITIES				SELECTIVE ADSORPTIONS				DIFFERENTIAL DIFFUSION			
		① GLYCOPROTEINS	Food Dispersed into Colloid Sols, Emulsions or Simpler Molecules which can Diffuse through the Gel		PROTEINS	FATS								
Molecules 0.2 - 5 m μ	Molecular (Chemistry)	Proteins Lipids Water Salts Carbo- hydrates etc.	ANALYSES AND SYNTHESIS OF NUMEROUS CHEMICAL INDIVIDUALS											
Atoms 0.1 - 0.6 m μ	Atomic (X-Ray Spectrometry)		CARBOHYDRATES ↔ AMINO ACIDS ↔ LIPINS											
Atomic Nuclei	Nuclear		OXIDATION-REDUCTION POTENTIAL											
Electrons	Electronic (Physics)													

① NERVOUS SYSTEM	② HORMONES	③ AIR	④ FOOD	⑤ TISSUES	⑥ TYPICAL CELL	⑦ ENZYMES	⑧ SENSES	⑨ PERIOD	⑩ SUMMATION	⑪ EVOLUTION
Automatic Sympathetic Parasympathetic Thoracic-Lumbar Bulbo-Sacral  Cerebro-Spinal Motor Sensory  Integrative Nuclear Cortical	See Table of Hormones	Quantity Quality Purity Sufficient to Supply Oxygen Evaporation at Skin (Cooling Effect)  Absence of Excess CO <sub>2</sub> CO <sub>2</sub> CO (A certain amount of O <sub>2</sub> is essen- tial to sti- mulate the respiratory center, etc.)	Quantity, Quality Variety Sufficient to Supply Adequate Water Salts NaCl, PI, I Fats Carbohydrate Proteins  (Must include all essential Amino-Acids) Roughage Vitamins  See Table, of Vitamins	Specialization  ORGANS Specialization  Adaptations Due to Special Positions	Cell Wall or Interface Cytoplasm Nucleus Chromosomes Centriomeres Genes Genels Golgi-System Mitochondria  Specializations Due to Special Positions	Salivary Ptyalin Stomach Pepsin Pancreas Trypsin Diastase Steapsin  Liver Lipase Diastase  Gut Entero-Kinase Steapsin Respiration Ferment in Man=Fe Compounds Horse Shoe Crab=Cu Compound Phallusia= V Compound (With Free Sulphuric Acid in the Blood)	Sight Hearing Smell Touch Taste Vestibular (Balance)  Special Sense Receptors  Pain Temperature Vibration Proprioceptive Epicritic	Function Influences Structure  ADULT PERIOD  Structure Influences Function  "As the twig is bent so is the tree inclined"	The Summation of the Structural and Functional Systems (indicated by the Greek Σ) into Health through Integration (indi- cated by the Integration sign //) Normal Physiology: into Disease or Death through Abnormal or Pathological Physiology	Moleculon First Life (Hypothesis) Genes Filterable Vir Genes or Groups Bacteria (Bacteriology; Mildews Molds, etc. Monocellula; Plants and Animals Multicellula; Plants and Animals

acetic acid with glycine and eliminate it as phenaceturic acid. Sherwin (1917) found that *man* couples this latter poison with glutamine, eliminating it as phenylacetylglutamine. Dr. F. W. Power (Fordham University) found that the *chimpanzee* eliminates phenylacetic acid in the same manner as man (Proc. Soc. Exp. Biol. Med. 1936, 33, 598).

*Turgidity of the Bio-colloids.* The bio-colloids consist of carbohydrates (starch, cellulose, glycogen), proteins (albumins, globulins, ossein) and lipoids (lecithin, cholesterin, fats and oils). Each tissue has a normal state of swelling or turgor, which is greatly influenced by the effective reaction (acid if  $\text{pH} < 7$ , alkaline if  $\text{pH} > 7$ ) and by salts. The swelling is least at or near the isoelectric point; its increase by both acids and alkalis soon reaches a maximum, after which it falls again. Neutral salts oppose the action of acids and alkalis, apparently by driving back their ionization, and thus bringing the effective reaction (H-ion concentration, pH value) nearer to the isoelectric point. So sensitive are colloids to minute changes in reaction detectable only potentiometrically or by the use of very delicate indicators, that fibrin will easily distinguish by a big difference in swelling, between conductivity water and ordinary distilled water, which contains  $\text{CO}_2$  and has a pH of about 5.5. For effects of climate and weather, see p. 168.

It must be remembered that the isoelectric points of the proteins are not at neutrality ( $\text{pH} 7$ ) and differ among themselves (see p. 300). Furthermore, many biological structures (tissues) comprise several proteins in their make-up and therefore show swelling phenomena which represent a composite effect. (See p. 404.)

If the *oxidation processes of the body* are normal, the hydrogen in foods is oxidized mainly to water, and the carbon mainly to carbon dioxide—a gaseous acid which is exhaled without demanding protein or fixed alkali of the organism for its elimination. Nearly two pounds of caustic soda would be required to neutralize the acid produced daily by the average adult. In cases of pathological oxidation, as in diabetes, dextrose (glucose) accumulates in the blood beyond the normal average of less than 0.1% (hyperglycemia), exerting a dehydrating or shrinking action on the tissues, while fats are oxidized only partially to the poisonous acetone, diacetic acid, and beta-oxybutyric acid,



which may produce "acidosis," really a diminished alkalinity recognizable by the fact that an abnormally large quantity of sodium bicarbonate is needed to render the urine alkaline. As the body colloids are thus forced nearer to their isoelectric point, their water-holding capacity diminishes, "free" water appears in the blood, and the patient shrinks. In fact, throughout life there is a continual syneresis of the body colloids: compare the chubby hand of an infant with the shrunken hand of an old man. (See p. 148.)

Local accumulation of acid may cause swelling (*edema*); for example, insect stings which may be simulated by "stinging" gelatin with a needle dipped in acid. If fluid accumulates in an organ, having a rigid capsule (eye, kidney), the swelling tends to establish a vicious circle (glaucoma, nephritis) by compressing the blood vessels and cutting down the alkaline blood stream, which is unable to absorb and wash out the acids (mainly  $\text{CO}_2$ ) formed by living protoplasm. The degeneration of the kidney in these circumstances is so typically one of the colloidal swelling and coagulation that the physician judges the condition by the microscopic appearance of the casts (hyaline or granular) sloughed off by the tubules. Certain infections (scarlet fever, for example) produce substances likewise harmful to the kidney tissue. See "Edema and Nephritis," by Prof. M. H. Fischer, (University of Cincinnati).

The relation between the clinical, pathological, and colloid chemical pictures or complexes in inflammation has been diagrammatically illustrated by Prof. H. Schade (Münchener med. Wochenschr. 1924, No. 1, pp. 1-4) as follows:

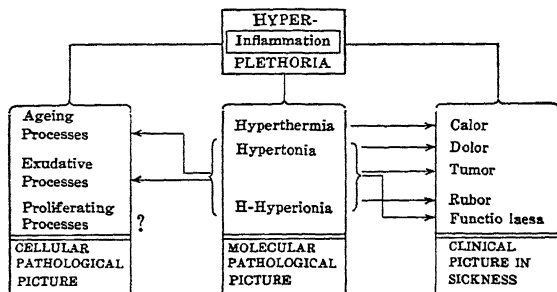


Fig. 41. Diagrammatic representation of inflammation, (H. Schade).

Owing to increase in quantity of dissolved substances, the osmotic hypertonia may reach as high as 11 atmospheres, while H-hyperionia may result in a hydrogen ion concentration 50 times normal.\*

#### CAPILLARY CIRCULATION AND DIFFUSION †

Some notion of the enormous surfaces afforded by the capillaries for diffusional interchange between blood and tissues may be gathered from Krogh's estimate ("The Anatomy and Physiology of Capillaries," 1st ed., 1922, p. 10): "Supposing a man's muscles to weigh 50 kg. and his capillaries to number 2,000 per sq. mm., the total length of all these tubes put together must be something like 100,000 kilometers or  $2\frac{1}{2}$  times round the globe and their total surface 6,300 sq. meters." (about  $1\frac{1}{2}$  acres). Capillaries form an exceedingly complex system interposed between two other complex systems, blood and tissues, all striving toward a kinetic equilibrium. Not only are capillary structure and conditions different in different animals, but also in different parts of the same animal and even within the length of a single capillary. It must be realized, therefore, that only general tendencies can be here referred to. For further details the following may be consulted: "The Capillaries of the Skin and Their Responses," by Sir Thomas Lewis (University of London); "The Anatomy and Physiology of Capillaries," by Prof. August Krogh (University of Copenhagen, Nobel Laureate), 2nd ed., 1929; and "Capillary Pressure and Capillary Permeability," by Prof. Eugene M. Landis (University of Pennsylvania), *Physiological Reviews*, 1934, 14, 404-481.

The remarkable work of A. Krogh and his collaborators shows that for the most part the capillaries intermittently open and close. They thus act practically as tiny railroad sidings, along which the red blood corpuscles are shoved in single file like tiny trains of freight cars. When the motion stops, oxygen diffuses slowly into the surrounding tissue served by the capillary, while carbon dioxide diffuses about 30 times more rapidly to the red blood corpuscles. When the exchange reaches the proper

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\* This means a pH of between 5 and 6, which is about the acidity of ordinary distilled water not protected from CO<sub>2</sub> absorption.

† The author is indebted to Prof. E. M. Landis (Univ. of Penn.) for some critical suggestions.

balance, the capillary opens, and the arterial pressure forces the little freight cars, now loaded with carbonic acid, into the venules, their places being taken by new oxygen-containing corpuscles. Cyanosis (*e.g.*, turning "blue" with cold) follows a stasis in the skin capillaries, succeeded by a loss of oxygen and a gain in  $\text{CO}_2$  by the red blood cells as the "arterial" blood becomes "venous."

Underlying these apparently simple microscopically visible changes are many factors, chief of which seem to be the following:

(1) *Hormonal or Endocrine Control.* The posterior lobe of the pituitary yields to the blood a very potent hormone which exercises capillary control. Krogh thinks it regulates the tone of the tiny Rouget cells which embrace most capillaries; for in the frog, extirpation of this lobe causes an edema which he says is due to the relaxation of the Rouget cells. Krogh estimates that this hormone is effective in less than one part in one hundred million, while Abel has isolated a purified hormone said to be effective one part in 18,750,000,000.

(2) *Nervous Control.* There exists both a psychic nervous control ("blushing," turning pale), and a vasomotor (sub-conscious) control. Light exercises a lasting effect on the reactivity of capillaries to stimuli (work of Finsen).

(3) *Turgidity Control.* A variation in the degree of swelling or turgidity of the tissue colloids comprising the capillary wall or surrounding the capillary, would obviously result in the opening or closing of the capillary and it would seem easy to explain the process by assuming that when the tissues accumulate carbonic acid, they swell and close down on the capillaries, relaxing again as oxygen comes in and carbonic acid diffuses out to the red blood cells. The tissues would thus automatically tend to regulate their supply of blood in accordance with their demands; and in fact Krogh found that in exercising muscle many more and larger capillaries are open than in quiescent muscle. If anything prevents the capillary from opening again at the proper time, we have a vicious circle—an "acid" capillary surrounded by "acid" tissue—leading to congestion or inflammation.

Krogh stated (1st ed., pp. 131-133) that change in pH (H-ion concentration) does not seem to be the dominant factor in capillary control but that this control is associated in some way with a lack of oxygen. Krogh however estimated the pH from

the  $\text{CO}_2$  tension, a method open to objections because of the many other factors which may influence the H-ion concentration of tissue, *e.g.*, the presence of buffer salts and proteins, and selective diffusion between the plasma and corpuscles. Eliot R. Clark and Eleanor L. Clark (Anatomical Record, 1924, 27, 200) found capillaries in a tadpole's tail which probably did not lack oxygen because of the thinness of the tissue, but which nevertheless automatically opened and closed, as did also segments of capillaries between Rouget cells.

It seems difficult to determine these microscopic and minute fluctuations in pH but a technique may yet be developed.\* As Krogh says (p. 134), it is "a case for renewed investigation"; but it is hard to forego the belief that *variation in the swelling of tissue*, associated with fluctuation in H-ion concentration and the amount of products of metabolism, is a factor in the control of capillary circulation. However, this view lacks unequivocal proof.

#### ULTRAFILTRATION THROUGH CAPILLARIES

While the capillaries of some organs (*e.g.*, liver) *normally* permit the passage of colloidal substances, and while in cases of disease (*e.g.*, nephritis, with albuminuria) colloids may pass, in general the thin capillary wall, composed of a single layer of endothelial cells, is practically impervious to colloids, though highly permeable to crystalloids. Landis found that fluid filters through a frog's capillary 100 times more rapidly than through the membrane of a human red blood cell and over 3,000 times more rapidly than through the membrane of a sea-urchin egg.

Although the total osmotic pressure of the blood plasma is about 7 atmospheres, as far back as 1895-6 Prof. Edward H. Starling (University of London) found that the *colloid osmotic pressure* of the plasma (that is, the *oncotic pressure* or "inward suction" exerted by the plasma colloids alone) amounted to only about 30 mm Hg, because the capillary membrane was completely permeable to the crystalloids. Starling postulated a balance between this small colloid osmotic pressure and the capillary pressure which he deemed to be of the same order of magnitude, so

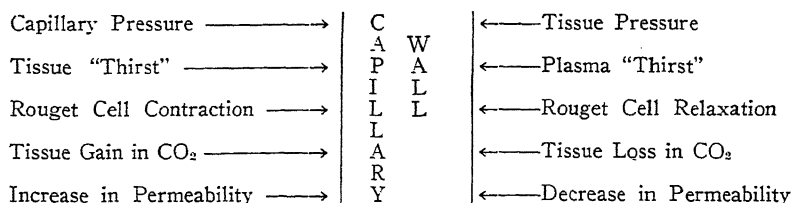
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\*Prof. Robert Chambers (N. Y. University) has been able to inject pH indicators into an amoeba and even into its nucleus. See his paper in Alexander's "Colloid Chemistry," Vol. II (1928).

that fluid would pass into the tissues where the capillary pressure dominates and back into the blood where the "colloid suction" of the blood dominates. At the arterial end of a capillary the blood pressure in man varies from about 28 to 65 cm H<sub>2</sub>O (average 43.5), while at the venous end it drops to from about 8 to 24 cm H<sub>2</sub>O (average 16.5).

The importance of the continual re-absorption of fluid which is continually passing through the capillaries is evident from the statement of Landis that at a capillary pressure of 10 mm Hg (about 1.35 cm H<sub>2</sub>O) it would take only about 10 seconds to drive a man's total plasma volume into his tissues, if human and frog mesentery capillaries are of like permeability and if no force held the fluid in the capillaries.

The capillary pressures are affected by many factors, *e.g.*, cardiac insufficiency (weakness of the heart), arteriosclerosis (hardening of the arteries), heart pulsation, contraction or relaxation of veins or arteries under the influence of drugs, nervous impulses, etc. Furthermore, the veins have in them valves of pouch-like nature, which permit blood to pass only toward the heart; so that any pressure on the veins, as by the muscles during exercise, must force the blood toward the heart (the "*venous pump*"). See "The Third Major Mechanical Factor in the Circulation of the Blood" by Prof. Yandell Henderson (Yale University), read before National Academy of Sciences ("Science, 1934, 79, 508-10). Thus, when our hands hang down for a while, their veins distend; but on opening and closing our fists several times, the swelling is relieved. Venous "back-pressure" and alteration in the permeability of the capillary wall also affect capillary pressure. The diagram below illustrates some of the main factors concerned in fluid transfer:



Though the physico-chemical laws of the Donnan equilibrium are concerned in the composition of the transudate while it is in equilibrium with the blood stream, deviations from the Donnan

equations occur because of the complexity of the system. Thus, ions may diffuse through the tissues according to their differing "activities", and no true equilibrium results. Landis concludes: "The movement of fluid through the capillary wall depends primarily upon balance between the capillary blood pressure and the colloid osmotic pressure of the blood. The effectiveness of this balance is modified, however, by endothelial damage, by tissue pressure, by temperature, by accumulation of metabolic products and by other unidentified factors."

### CONNECTIVE TISSUE

Prof. H. Schade (University of Kiel) regards the connective tissue of the body as a huge colloidal "organ" weighing about 20 pounds in adults, inserted between blood vessels, organ tissues and skin like a great clinging mantle. Three factors determine its swelling or water-holding balance: (1) a kinetic ionic "equilibrium" striving toward the normal of pH 7.45 and a molar ratio for Na:K:Ca of about 100:2:2; (2) a normal colloid-osmotic pressure in the blood serum; (3) normal compression due to the mechanical resiliency of its own and of surrounding tissues. Placed in a beaker of "physiological" solution, connective tissue will swell more than it does within the body, unless all these three factors are experimentally reproduced.

Schade points out that connective tissue consists of two separate substances (the matrix and the collagenous fibrils) which exhibit the swelling antagonism shown in the following table:

TABLE XXXII  
SWELLING ANTAGONISM IN CONNECTIVE TISSUE

Immersion in	Matrix	Collagenous Fibrils
Pure water	Swells greatly	Precipitation
Increasing NaCl concentration	Decrease in swelling	Increase in swelling
Acid solutions	Slight swelling	Swells greatly
Alkaline solutions	Swells greatly	Slight swelling

Since the swelling minima of the matrix and the collagen are not at exactly the same pH, there are zones in which these com-

ponents of connective tissue oppose each other's swelling; *e.g.*, in "acid" inflammation the water released by the matrix is readily taken up by the collagen which is "thirsty" under those conditions, with a net result that water tends to remain in the connective tissue, available both to cells and blood on sufficiently urgent demand.

### *Water Balance in the Body—Edema*

Prof. H. Schade considers the body as consisting of three great "domains": (1) the *connective tissue*, which is interposed between the other two; (2) the *blood*, separated from (1) by the capillary walls which function as a *dialytic* membrane; and (3) *the cells* whose walls function as an *osmotic* membrane. There is a *swelling antagonism* between connective tissue and cells, and a *water balance* between connective tissue and blood. In the blood itself there is a swelling balance between the erythrocytes (red cells) and the plasma proteins. The arterial pressure ultrafilters fluid through the capillary walls, and if a corresponding amount is not re-absorbed, fluid will accumulate and an *edema* come into evidence, increasing until the increased distention of the skin adds sufficient counterbalancing tissue pressure. Excess tissue fluid is also drained away by the lymphatic system, which discharges into the subclavian vein, *i.e.*, into the blood stream.

Very commonly in edema the tissues have so much "free" fluid that it can be aspirated off by insertion of a needle (ascitic fluid). Tissues may vary greatly in their capacity for taking up water, however, possibly because of differences in aggregation of their colloids or other structural units. Alexander (J.A.C.S., 1921, 43, 436) found that a 4 per cent solution of 200 mesh (100  $\mu$ ) karaya gum is a thick, viscous fluid adherent to a test-tube, whereas a 4 per cent solution of 20 to 30 mesh (1000  $\mu$ ) gum, looks jelly-like, slides readily in the tube, and allows free water to be extracted from it by a medicine dropper. With coarser gum particles, visible free water may be drained off. It appears that a condition of optimum colloidalilty in the tissues is one factor involved in edema.

Schade points out that edema may have a variety of origins: (1) Increase in swelling capacity of the tissues, as with alkali- and salt-edemas, especially those caused by iodine compounds;

(2) rise in oncotic pressure of the blood, as where diseased kidneys (see p. 412) do not remove sufficient water from the blood, so that the time or the zone of water-outgo from the capillaries is abnormally large, the time or the zone of water-intake (or recapture) being correspondingly reduced; therefore fluid accumulates in the tissue; (3) inflammation edema, due to osmotic hypertonicity in the tissue, or to chemical changes there; (4) edema caused mechanically, *e.g.*, by stoppage of the venous circulation. "Here the criterion is increase in the mechanical pressure of the blood in the venous section of the capillaries," with the same unbalanced fluid interchange as in (2). (See "Colloid Chemistry and Internal Medicine," by H. Schade, in Vol. II, Alexander's "Colloid Chemistry, Theoretical and Applied," pp. 629-649; also Krogh, *lib. cit.*, who states that the problem of edema is one of great complexity.)

#### EXTENSIVE SUPERFICIAL BURNS

It is well known that if about one-third or more of the total surface of the body is superficially burned, even though slightly, there is great danger of death. As Prof. Frank P. Underhill (Yale University) showed, this is due to a concentration of the blood, probably consequent upon an upset in the flow of fluid to the burned area and its re-absorption into the blood again. While blood concentration up to 125 per cent. of the normal value is not serious, life can not generally be prolonged when 140 per cent. concentration is reached. (See Alexander's "Colloid Chemistry," Vol. II, pp. 723-730.)

Normally, the capillaries (see p. 402) ultrafilter fluid into the tissues and further along or later on re-absorb a like amount, possibly because of pH change due to taking up CO<sub>2</sub>. In a burn, however, the nervous, hormonal, or other conditions are changed, and "water" remains locally, often appearing in "water-blisters." A child whose cotton flannel nightgown caught fire *inside* from a gas-heater, died despite the fact that the very extensive burn was very slight and caused no great pain. A small rather severe burn is not generally serious, unless it becomes infected or is in some special place.

Being suddenly confronted with more than twenty persons badly burned in a theater fire in New Haven, Dr. Underhill treated the *systemic* effects by the continued administration of



water, by mouth when possible, otherwise subcutaneously, intravenously, by rectum, etc., the amount varying from 4 to 8 liters per day for several days, until blood viscosity tests showed a drop to safe levels. Naturally, proper medical treatment of the burned areas was given, protection in these cases being effected by a spray of paraffin. Tannic acid is now also used. All these patients were saved, except one who was moribund on arrival at the hospital, although on the basis of earlier experience all would have been accounted bad risks. The severity of the cases was determined by blood viscosity tests.

Blood concentration may be produced in other ways, *e.g.*, by sweating, restriction of water intake, saline cathartics, too much salt, various drugs; but where the nervous mechanism is unaffected, liberal draughts of water will usually relieve the condition. With extensive burns, however, water administration must be kept up until blood viscosity drops to near normal.

### TRAUMATIC SHOCK

Many years ago Dr. Fenton B. Turck (see Dr. Turck's résumé in his book "The Action of the Living Cell," Macmillan, 1933) showed that if a cat's paw was ligated so that no blood flowed through it and was then crushed, the animal showed no sign of "shock" until the ligature was loosened so that blood from the injured part entered the general circulation. Sir Thomas Lewis (*lib. cit.*) showed that on injury there is released from tissue a small amount of what he terms "H-substance," because it has the same action as histamine in causing great relaxation of the smaller blood vessels. If the injury is sufficiently extensive, so much blood may leave the larger vessels that the arterial pressure drops dangerously, and the person practically bleeds to death into his own tissues. Where there is lack of human blood (the proper *type* is essential as was shown by Dr. Karl Landsteiner, Rockefeller Institute, Nobel Laureate), for transfusion, this form of circulatory shock is generally treated with intravenous injection of gum acacia (gum arabic), 6%, dissolved in 0.9% NaCl, since the gum has sufficient calcium and potassium salts. This procedure was originally suggested by Sir William Bayliss (University of London) in 1916, and it was instrumental in saving many lives during the great War. Krogh states (p. 367

of his book) that the gum should make "an almost ideal provisional substitute for blood plasma . . . if the shock has reached such a stage that the capillaries have become permeable to gum, the injection will prove useless." If it remains within the vessels, the gum solution exerts the same colloid oncotic pressure as plasma.

### DUST DISEASES—MEDICAL AND LEGAL ASPECTS

Comparatively recently much attention has been aroused by a disease known as "silicosis," a fibrosis of the lung often associated with tuberculosis, due to the frequent inhalation of dusts, particularly of silica and silicious minerals. It is estimated that dust particles 1 micron in diameter will fall in still air only about 6 feet in 8 hours, and particles five times as big require one hour to fall to the floor from the height of a man. Drafts, air currents, and sweeping, keep them up longer, and the fine and most dangerous dusts may never settle. Many manufacturers do not know of these hazards until haled into court by a negligence law suit, only to find that their insurance policy does not cover them.

Increasing attention is being given to dust removal. Here the important factor is *the amount* of dust that escapes, *not the percentage* which is caught. In many conditions the U. S. Bureau of Mines estimates (Information Circular No. 6848) that the collection efficiency must be over 99.998 per cent. Miners, quarrymen, potters and others have long been known to be subject to special ills, which have been referred to by Hippocrates, Pliny, Agricola and other ancient writers, and the mortality statistics, when properly analyzed, indicate greatly increased incidence of such diseases as "miners' phthisis," silicosis, asthma, etc., among those exposed excessively to dusts. (See further in "Dusts, Fumes and Smoke and Their Relation to Health," by Dr. Leonard Greenburg, in Vol. II of Alexander's "Colloid Chemistry," pp. 845-68).

### INFECTIVE DUSTS

In the ordinary course of conversation, colloidal particles, presumably of saliva, are ejected from the mouth and lips, being most marked in sounds involving a more or less explosive emis-

sion of breath—*e.g.*, with *b*, a consonant formed by stoppage of intonated breath at the lips; with *d*, a voiced dental stop; with *p*, a voiceless labial stop; with *s*, a dental fricative, formed by bringing the tongue near enough to the teeth to produce marked friction of the outgoing breath. These particles may be readily seen by passing a powerful beam of light in front of the speaker, especially in a darkened room.

That droplets coming from the mouth and nose, especially during conversation and sneezing, may be carriers of infection, has long been known; and all those assisting in surgical operations now wear protecting masks of gauze. An interesting older reference to a similar matter is given by Dr. James Ross' ("The Graft Theory of Disease," London, 1872, p. 30): Referring to the earlier proof by Dr. Angus Smith, Ross says: "I had a striking illustration of the fact that epidermic scales may be wafted in atmospheric currents in a case of confluent smallpox which I attended in November, 1868. When the patient was convalescent I was called one evening to see him, and a beam of sunlight coming through the window, fell upon his back as he sat by the fire. The light was scattered by myriads of epidermic scales. On the slightest movement clouds of these scales were seen to arise from his head and face, the heavier settling on his clothes, while the lighter danced in the sunlight. This observation made a deep impression on me at the time, but I did not recognize its full significance until I read Prof. Tyndall's experiments with the electric beam."

## CHAPTER XXII

### PHYSIOLOGY AND PATHOLOGY (*Continued*)

#### DIGESTION

CRYSTALLOIDS, such as sugars and salts, are diffusible through the semipermeable walls of the digestive tube, but fats and most colloidal foods must first be dispersed into a sufficiently fine state. The disintegration of proteins (meat, egg white) and of carbohydrates (starch) is effected through enzymes (pepsin, ptyalin, trypsin); while fats (either directly or after separation of their glycerin) are emulsified by the alkaline pancreatic juice. The presence of protective colloids such as mucin, cholesterin (in bile), and the like may account for some of the divergences between the behavior of natural and artificial digestive juices. Thus, membranes moistened with bile permit the passage of particles to which they would otherwise be impervious.\* Since all body fluids contain protective colloids, no chemical action can go on in the organism without being influenced by their presence.

#### ABSORPTION, SECRETION, EXCRETION

These are largely the results of selective adsorption by, and differential diffusion or ultrafiltration through, colloidal tissues and septa, accompanied by swelling and shrinking. Thus the blood is a circulating colloidal fluid which holds more water when in the "acid" or venous condition than it does when in the more alkaline or arterial condition. Tissues and organs well supplied with venous blood tend to absorb water (intestine); whereas those well supplied with arterial blood tend to give up (secrete, excrete) water (kidney). Since the blood is passing in a continuous stream, the process continues as long as the supply of water permits, or until the blood is in equilibrium with the tissues.

Conditions which decrease the capacity of the blood and tissues to hold water (diuretics, hyperglycemia and acidosis in

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\* For discussion of this view, see "The Absorption of Fats" by F. Verzár in *Nutrition Abstracts and Reviews*, 1933, 2, 441. See also J. Alexander, "Some Colloid-chemical Aspects of Digestion, with Ultra-microscopic Observations," Jr. Am. Chem. Soc., 1917, 39, 89. See also p. 126 for analogous phenomena in filtration.

diabetes) naturally result in the elimination of the excess or "free" water (polyuria, diarrhea).

*Minute* quantities of acid increase the swelling capacity of colloids, which quickly reaches a maximum; after which increasing acidity causes shrinking. Neutral salts oppose the action of acids apparently by driving back the ionization of the acid and thereby reducing the H-ion concentration which is an important factor, but by no means the only one.

The functioning of organs is largely controlled by nervous influences. Thus, a sudden nervous shock by causing vaso-dilation may send an excessive supply of arterial blood through the mesenteric arteries (in effect an "internal blush"), and cause secretion into the intestine (nervous diarrhea).

It must not be forgotten that the introduction into a cell of abnormal substances may upset its regular catalytic syndrome or behavior, and result in a great increase in outwardly diffusible material, *e.g.*, as when cells are activated by hormones. Bacteria attacked by bacteriophage seem to swell up and burst. Lead tends to be stored in the bones as an insoluble phosphate; but if such a "plumbized" person is given iodides, the lead is set free as the very soluble lead iodide, and acute lead poisoning may supervene. Beyond a certain dose, mercury slays relentlessly, being fixed by the kidneys and causing a slow, irreversible coagulation of the cell colloids and/or inhibition of the cellular catalysts.

Hydrolyzable salts are readily split up upon diffusion through a colloidal gel. Thus, ferric chloride upon diffusion through agar or gelatin gel yields ferric hydroxide which is selectively held back and hydrochloric acid which differentially diffuses ahead. If a little potassium ferrocyanide and alkaline phenolphthalein be added to the colloid gel, the latter will soon be banded in patriotic red, white, and blue (see p. 118). Depending upon the structure of an organ, the location of its cavity, its arteries and veins, and its outlet, it may yield an acid secretion (gastric juice) or an alkaline secretion (pancreatic juice). Individual substances or mixtures in the blood stream or other body fluids may be selectively separated or concentrated.

An insight into the complexity of these processes may be had by considering the functioning of the kidney. Its Malpighian tufts are plentifully supplied with arterial blood containing "free"

water; but since the interior diameter (lumen) of the afferent vessels is less than that of the efferent vessels, a "back pressure" is produced which the heart-throb makes a slight pulsating pressure, causing the tufts to act as an ultra-filter and pour a copious but very dilute ultrafiltrate of the blood into the convoluted tubules. The tubules, however, have a plentiful supply of venous blood, which is unsaturated with water and re-absorbs most of it together with some of the substances contained in the preliminary secretion; so that the concentrated excretion (urine) that finally

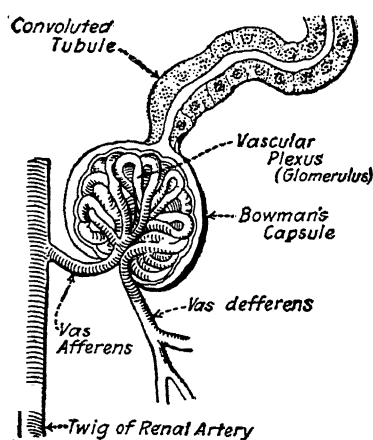


Fig. 42. Glomerular Structure.

drips into the pelvis of the kidney has in solution many substances found in the blood, but in totally different concentrations. Bechhold estimates that the average of two liters of urine voided daily by a man represents a preliminary secretion of fifty liters, forty-eight being re-absorbed within the kidney itself. (Fig. 42.)

### HEALING OF WOUNDS

In general this process depends on the formation of a fluid exudate or transudate (sol) which later sets to a gel, cementing together the severed surfaces. Within this gel the severed nerves tend to push their dendrites (see C. C. Speidel, references on p. 434), and new capillaries or other organized vessels tend to form (see R. C. Parker, "The Development of Organized Ves-

sels in Cultures of Blood Cells," Science, 1933, 77, 544-46). The exterior portion may dry up and fall off as a "scab," while under the scab shrinking and desiccation lead to formation of scar tissue. Since scar tissue and normal tissues swell and contract differently with changing conditions, changes in the weather frequently produce tension on the nerves embedded in scar tissue, which causes pain.

Larrey, celebrated surgeon of the Napoleonic era, observed that the presence of the larvae of flies facilitated the healing of wounds. In 1930 Dr. Wm. S. Baer (Baltimore, Md.), used clean fly-larvae as healing agents in wounds and in osteomyelitis. In 1912 Macalister used as a healing agent an extract of the plant *comfrey* (related to *heliotrope*), which contains *allantoin*, a substance discovered in 1799 in the amniotic fluid of cows by Vauquelin (Muséum de Paris). Synthetic allantoin was also found useful, and this substance is produced by fly-larvae. An allied substance, *urea*, is also said to be useful as a healing agent.

#### IMMUNOLOGY AND SEROLOGY \*

It has long been known that, with some diseases, one attack can render a person *immune* to subsequent attacks; but it is only comparatively recently that the nature of the protective or immunizing mechanism was discovered. However, as early as the 7th century, A.D., the Chinese were inoculating from person to person to protect against smallpox, and a whole century before Jenner's discovery of vaccination they were using cow-fleas (an insect carrier) to give a protective attack of cowpox. (See J. Alexander, Science, 1936, 83, 230.)

The relatively modern science of *immunology* enlists the co-operation of specialized groups of physicians, bacteriologists, and chemists. Practically it dates from Louis Pasteur, who discovered how to immunize against the dreaded anthrax and rabies. Joseph Meister, the first person to be saved from rabies by Pasteur, is concierge at Institut Pasteur at Paris, a living monument to the master chemist-bacteriologist-immunologist.

The precise chemical nature of the colloidal substances involved in immunological reactions being unknown, they were

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\*I am indebted to Dr. Karl Landsteiner for some critical suggestions.

given names based on their observable effects. This has led to the development of a special nomenclature, which must be here outlined.

*Antigens* are substances which can stimulate an organism (animal or plant) to produce other substances, termed *antibodies*, which are capable of reacting specifically with the inciting antigen. The antigen must be introduced under proper conditions, and time is required for the production of the antibody, or *immunization*, as it is called. Apart from the *immune antibodies* arising from presence of the antigen, the blood may hold more or less natural or *normal antibodies* for some antigens. Most antigens are proteins with large colloidal molecules; but gelatin (which lacks tyrosine and tryptophane, both of which contain aromatic or benzene rings), and protamines (which are mainly complexes of diamino acids) do not serve as antigens.

*Toxins* are *poisonous antigens*—for many antigens, *e.g.*, egg-white, casein from milk, etc., are not poisonous in immunizing amounts. The antibody evoked by a toxin (that is, a toxin antigen) is called an *antitoxin*. Substances like arsenic, strychnine, morphine, which do not induce the formation of antibodies, should be called poisons, not toxins.\* Where a bacterium, on breakdown, gives rise to a poisonous antigen, this is termed an *endotoxin* (*e.g.*, typhoid bacillus), in contradistinction to extracellular *exotoxins* which are excreted by other bacteria, *e.g.*, diphtheria and tetanus bacilli. *Snake venoms* and the highly poisonous *toxalbumins*, ricin (from the castor bean) and abrin (from the jequirity bean) generate specific antibodies. Some toxins can be altered chemically or physically so as to lose their toxicity, though they are still capable of evoking antibodies, *e.g.*, when diphtheria toxin is treated with formaldehyde and alum. Such a modified toxin is called a *toxoid*, and its activity may be due to the slow regeneration or solution of the original toxin.

*Synthetic Antigens.* Dr. Karl Landsteiner (Nobel Laureate, Rockefeller Institute for Medical Research) found that when organic substances of known chemical constitution were coupled

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\* As pointed out by Prof. J. J. Abel, the Greek word *toxikon* originally meant "of or belonging to the bow," and in this sense the root survives in the word *toxophilite*, a lover of the bow, or of archery. The word was carried over to the arrows shot from the bow, and also to the poison with which the arrows were usually imbued.



to proteins by diazotization,\* the compound thus formed could evoke the production of antibodies, but the specificity depended mainly on the *haptens*, as Landsteiner termed the molecule attached to the protein. Free haptens, of themselves, are incapable of evoking antibody formation. (See p. 370 on the vitamin-enzyme relationship.) Apparently, the free fields of force of the hapten are determinative of specificity, a view supported by the fact that haptens closely alike chemically interact serologically (crossreactions).

*Antigen-Antibody Reactions.*—The chief immunological reactions may be grouped under one of the following heads:

(1) *Toxin-antitoxin neutralization*—a proper mixture of toxin and antitoxin is innocuous. Antitoxin, *if administered in time*, can neutralize a toxin formed in or administered to an animal. But if diphtheria antitoxin is given after the toxin has been fixed irreversibly by certain nerve cells in the medulla, death may inexorably follow as the heart and respiratory system become paralyzed; even in cases that recover, temporary paralysis of the limbs is sometimes seen. Modern practise is to immunize children by injections of toxoid or of toxin-antitoxin mixtures. As far back as 1909, Dr. J. G. M. Bullowa and the writer observed in the ultramicroscope the mutual coagulation of the toxins of diphtheria and tetanus by their respective antitoxins, noting that only the specific antitoxin produced the effect.

(2) *Precipitin reactions* depend on the fact that when a soluble antigen is added in proper amount to the blood serum of an animal immunized by injections of this same antigen, a visible precipitate is formed. The flocculation method for the titration of both toxin and antitoxin was worked out by G. Ramon (Compt. rend. Soc. biol., 1922, 86, 661, 711, 813; Ann. Inst. Pasteur, 1923, 37, 1001). For details of the Ramon test, see, *e.g.*, Stanhope Bayne-Jones in Jordan and Falk's "The Newer Knowledge of Bacteriology and Immunology," Univ. of Chicago, 1928.

(3) *Agglutination reactions* are characterized by the fact

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\* Typical of the substances coupled to the protein are metanilic acid (*m*-aminobenzenesulfonic acid) and aminobenzoic acid. On treatment with nitrous acid, the amino group yields the extremely reactive diazo group,  $-N=N-$ . This diazo reaction, as it is called, is largely used in link or couple together substances to form dyes or colors; *e.g.*, para red is made by diazotizing *p*-nitraniline and adding  $\beta$ -naphthol. A wide range of substances have been used by Landsteiner. See his book, "The Specificity of Immunological Reactions," C. C. Thomas, 1936.

that when an antigen in the form of visible particles (*e.g.*, bacteria, red blood cells) is mixed with its corresponding antiserum, the particulate antigen forms flocs, or agglutinates. The flocs usually settle out. If the antigen consists of motile cells (*e.g.*, typhoid bacilli, sperms), these can be seen to cohere or agglutinate; and though their independent motility is lost, individuals in the group may continue for a time to show some motion. "Evidently these two reactions (agglutinin and precipitin) are very closely related, the differences depending entirely on the size of the colloidal complex serving as antigen, and there is much reason to believe that precipitins and agglutinins are identical." (H. Gideon Wells, "The Chemical Aspects of Immunity," 2nd ed., 1929, p. 23). The ultramicroscopic observations above referred to indicate that antitoxins are also "precipitins," for they precipitate or coagulate their corresponding toxins or "precipitinogens" (precipitate formers). The Widal test for typhoid depends on the fact that blood serum containing typhoid immune bodies (that is, serum from a patient who has, or has had, typhoid) agglutinates live, motile typhoid bacilli—and furthermore, it dissolves them, or causes lysis, which will now be considered.

(4) *Lysis* (solution) is the term used by immunologists where immune serum has the power of dissolving or disintegrating a particulate antigen—*bacteriolysis*, where bacteria are dissolved; *cytolysis*, for cells; *hemolysis*, for blood corpuscles. Antibodies that produce lysis are called *lysins*.

*Complement or Alexin.* If an immune serum capable of causing lysis of cholera vibrios is heated for 15 minutes at 55° C., its lytic power vanishes, but returns again if some unheated, non-immune serum is added. This indicates that besides the specific lysin, both immune as well as non-immune sera contain another factor essential to the bactericidal, lytic action. Prof. Jules Bordet (University of Brussels, Nobel Laureate) applied the term *alexin* (from a Greek word meaning *helper*) to this second factor; Prof. Paul Ehrlich (University of Berlin) called it *complement*.

*Antibody Formation.* The present evidence indicates that antibody formation *takes place* within the cells, though the antibodies are *sought* for mainly in the body fluids, *e.g.*, blood serum, where they are largely found. If an immunized animal is bled,

*e.g.*, as when immune horse blood is taken to extract from it diphtheria antitoxin, a new supply of antibody soon reappears in the blood, apparently coming from the cells. A small amount of antigen can, therefore, produce a large amount of antibody, much more than could possibly be accounted for by the assumption that the molecules of the antigen enter, of themselves, into the antibody.

These and other facts led the writer to following concept of the *mechanism of antibody* production (Protoplasma, 1931, 14, 302-4):

There is a "*formation, within the cells themselves, of new specific catalysts which are able to direct the formation of antibodies*". Three possibilities present themselves as to the method whereby specific antigens produce specific catalysts which in turn determine specific antibody formation: 1, modification of a gene; 2, modification of a non-genic catalyst; 3, fixation of the antigen particle by a non-catalyst cytoplasmic particle in such a manner that the combination functions as a specific catalyst. Nature may utilize any or all of these methods, and perhaps others not thought of at present.

"All three of these possibilities involve the idea that the antigen *becomes an essential part of the directive surface of a catalyst particle*, which would tend to determine the formation of particle groups *having essentially the reverse of the electrostatic charge pattern* of the active catalyst surface and therefore of the antigen, or else of particle groups which *can acquire essentially such a reverse pattern* when they are detached and removed to some other part of the organism. Changes in hydrogen ion or other ion concentration might readily account for such detachment and changes, which could be in the nature of an electroversion. In its simplest form this concept may be illustrated by the diagrams,\* Fig. 43, wherein positively charged areas are represented as depressions below, and negatively charged areas as elevations above the dotted line representing neutrality. The applicability of Emil Fischer's well-known analogy of lock and key, which he applied to the fitting of enzyme to substrate, is at once manifest.

\* The actual fields of force extend in three dimensions. On the exterior area of the moulded layer or film may appear areas identical in pattern with those of the antigen—see p. 385.

That such an antibody particle would tend to unite with particles of its specific antigen, seems obvious; and the neutral units would tend to flocculate if conditions would permit—presence of precipitating ions, absence of colloidal protectors.”

The effectiveness and lasting effect of minute quantities of antigens becomes comprehensible on the basis of this view, for in theory at least, one single molecule or colloidal particle would be sufficient to convert a cell or an extracellular catalyst into a potential producer of a specific antibody. Furthermore, there is no reason why large numbers of different antigens may not simultaneously or successively affect the same cell with its many thousands of genes and other catalyst particles—which corresponds to the experimental facts. As long as the antigen-catalyst complex continues to function to produce the specific antibody, so

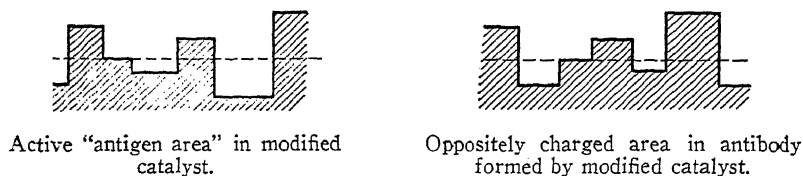


Fig. 43.

long will the production of immune bodies continue, despite bleeding. Variations in the *duration of immunity* \* would correspond to variations in the persistence of the antigen-catalyst complex, while inability to establish immunity would indicate non-formation of such a complex, or subsequent destruction of the antibody formed. All these phenomena appear in vaccinations, which has become a general term indicating inoculation with an antigen with the hope that immunity will result.

*The Nature of Antigen-Antibody Reactions.* Out of the efforts to explain the diverse and often confusing phenomena appearing in immunological reactions, there arose an unfounded and totally unnecessary antagonism between those who attempted to explain all of them on the basis of simplified concepts of colloid chemistry, and those who could see in them nothing but applica-

\* With smallpox immunity usually persists for many years, even for life, while with typhoid immunity may last but a few months,

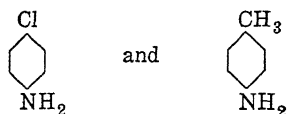
tions of the stoichiometric laws of classical chemistry, which had been developed from observations on the behavior and reactions of relatively simple substances. Nature does not order the interrelations of particulate units to meet the pedagogical necessities of propagandists of this or that school. The single phenomena have both chemical and physical aspects, and part of the whole truth lies in each aspect.

There is no room to consider here the immense literature dealing with the experimental and the theoretical aspects of the long conflict between the exponents of the chemical and the physical views of immune reactions.\* In epitome it may be said that Prof. Paul Ehrlich believed that they were purely chemical, resembling the combination between a strong acid and a strong base. Arrhenius and Madsen, however, suggested that the reactions resembled that between a weak acid and a weak base (*e.g.*, boric acid and ammonia, which on mixing reach an equilibrium wherein the amount of neutral salt, free acid, and free base are fixed according to the law of mass action—a view experimentally maintained by Heidelberger and Kendall (M. Heidelberger and F. E. Kendall (Columbia University), *J. Exp. Medicine*, 1935, 61, 559-591; 62, 467-483, 697-720). On the other hand, Prof. Jules Bordet considered immune reactions in the light of mutual precipitation of oppositely charged colloidal particles, later regarded as due to adsorption.

Dr. J. R. Marrack ("The Chemistry of Antigens and Antibodies," 1934, British Medical Research Council Report No. 194) gives an excellent review of both the chemical and the physical aspects of immune reactions. When a simple hapten combines with an antibody, as a rule no further reaction (*e.g.*, precipitation) occurs (J. Marrack and F. C. Smith, *Brit. J. Exp. Path.*, 1932, 13, 394). Therefore "it is possible to distinguish two stages in an immunity reaction: (1) specific combination of the 'determinant groups' with antibody, (2) secondary reaction—precipitation, agglutination, etc." Not only do many "determinant groups" lack chemically reactive radicals, but such groups having different chemical composition may be immunolog-

\* Much of this is summarized in "The Chemical Aspects of Immunity," 2nd ed., 1929, by Prof. H. Gideon Wells. See also Jordan and Falk, "The Newer Aspects of Bacteriology and Immunity," 1927; Arrhenius and Madsen, "Immunochemistry," 1907.

ically equivalent, indicating that they combine equally with the same antibody. This is the case with the groups



"Such a result can only be due to intermolecular forces and the specific character must be ascribed to (1) an appropriate distribution of polar fields on the 'determinant group' and on the antibody; and (2) to purely spatial considerations, since the approach of a 'determinant group' to a receptive site on the antibody may be prevented by an inert substituent which gets in the way (*steric hindrance*). These are the same factors as determine the specific selection of the molecules which are built into a crystal."

It is illuminating to consider a few instances where molecules are adsorbed by surfaces formed of molecules of quite a different nature, because of a mutual attraction of polar forces (free electronic fields). Nellenstein found (quoted by J. A. Garner, Trans. Faraday Soc., 1926, 22, 459) that diamond would adsorb methylene blue but not succinic acid; whereas graphite which differs from diamond only in the spacing of the carbon atoms, adsorbs succinic acid but not methylene blue. Prof. W. G. France (Colloid Symp. Mono., 1930, 7, 59) found with two complex diazo dyes which differed only in the location of their sulphonic groups, that one was adsorbed on the cube faces of potash alum, while the other was not.

Pointing out that specific adsorption can occur between isolated molecules as well as at surfaces, Marrack adds: "It will become progressively more important with the increasing size of the molecules concerned, because the firmness of union by polar forces and the possibility of a varied mosaic of polar fields increase with increasing molecular size. If the adaptation of one rigid \* molecule to another in solution in water involves the distortion of one or both, adsorption is not likely to occur, because their polar fields can be satisfied by the free water molecules without the necessity of distortion. On the other hand, if two

\* The rigidity of a molecule is mainly determined by the formation of rings, which may be joined either by chemical links or by attraction between polar groups.

suitable polar groups are held in proximity, their polar fields may neutralize each other and lose the attraction for water on which the solubility of the molecule depends."

It must be noted here that time is a factor in these reactions, and that with increasing particle size which accompanies increasing chemical complexity, there is a corresponding *drop* in particulate kinetic activity which, up to a certain point (see p. 43), favors the proper "seating" of one surface or area to another.

Since the stability of a suspension is governed by the balance between the attraction of its particles for water and for each other, as well as by the surface potentials of the particles, it is obvious that fixation of an antibody by an antigen may so alter this balance and the surface potential, that aggregation and flocculation will follow. Dr. Harold A. Abramson ("Electrokinetic Phenomena and their Application to Biology and Medicine," 1934, Am. Chem. Soc. Mono. No. 66) states: "We may expect the stability of bacterial suspensions to depend upon the magnitude of the forces which oppose the formation of aggregates. The aggregation forces are taken as (1) the usual cohesive or molecular forces and (2) those due to chemical reactions of special surface groups. Stabilizing forces probably depend in a complex way upon:

- (1) the  $\zeta$ -potential
- (2) hydration
- (3) the concentration of salt by varying the field strength in the electrical double layer.

But evidently a suitable theory is lacking."

Heidelberger and Kendall (M. Heidelberger and F. E. Kendall, J. Exp. Med., 1935, 61, 559-91) state: "The precipitin reaction between the specific polysaccharide of Type III pneumococcus and homologous antibody formed in the horse can be accounted for quantitatively by assuming the chemical combination of the components in a bimolecular reaction, followed by a series of competing bimolecular reactions which depend on the relative proportions of the components. These reactions would lead to larger and larger aggregates until precipitation ultimately occurred." They also found that this "quantitative theory of the precipitin reaction based on the laws

of classical chemistry to apply to an azoprotein-antibody system and to the crystalline egg albumin-antibody system (J. Exp. Med., 1935, 62, 467-83, 697-720). Their calculations are based on application of the mass law formula, which also underlies the "solubility product" principle according to which analytical chemistry is now taught.

Regarding the applicability of the law of mass action in cases like this, Marrack states (*lib. cit.*, p. 122): "In the kinetic derivation of the law of mass action no assumption is made as to the mode of union of the molecules that combine, except that the combination is reversible. It should therefore be applicable when molecules are joined by intermolecular forces. When, however, aggregates of molecules of continuously varying composition can be formed, and secondary reactions take place, the conditions may become too complex for its application." Heidelberger and Kendall (see above) met this objection by assuming a series of competing bimolecular reactions. Marrack further states: "In cases in which the antigen-antibody compound becomes irreversible it is obviously impossible to apply the law of mass action. It must be realized that with the complexity of the possible reactions involved it is unlikely that an equation will be found sufficiently general to fit all reactions. In these discussions the assumption is usually made, without warrant, that the antigen molecules or particles and the antigen molecules in a given reaction are homogeneous with regard to number of combining sites and dissociation constants of the combination at these sites. Now death rates and behavior with simple hemolysins indicate that bacteria and red blood corpuscles are not homogeneous. It is only with purified antigens such as crystalline egg albumin and polysaccharides, that homogeneity can be assumed. It is desirable that such antigens should be used in all work on theoretical aspects of the subject. The existence of agglutinoids\* shows that even the antibody molecules in a given serum need not be uniform in their ability to agglutinate."

That the mass law equations are not valid for "non-ideal" solutions (that is, those where forces act between the molecules or ions), is pointed out by Prof. Charles A. Kraus in his recent Willard Gibbs Medal Address (J. Chem. Education, 1935, 12,

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\* Agglutinoids are substances which combine with agglutinin without producing agglutination.



568). "A complete understanding of electrolytic phenomena will be arrived at only when it is known how the properties of electrolytes vary with (and depend upon) the fundamental constants of the media in which they are dissolved. . . . If undissociated molecules of electrolyte exist in solution in a non-polar medium, we must not look upon such combinations as chemical compounds in the ordinary sense. The forces that hold the ions together in the ion pairs, or their more complex aggregates, are electrostatic rather than chemical."

Considering the multiplicity of factors operative in immunological phenomena, it is hardly to be expected that any one simple relation can dominate them all. We must distinguish between what actually *does* happen in any particular case, and what *might have* happened or *can be made* to happen under other controlled conditions.

#### ALLERGY AND ANAPHYLAXIS

The term *allergy* (from *allos*, altered, and *ergia*, reactivity) was introduced by von Pirquet and adopted by Doerr to indicate any deviation from normal reactivity, whether an increase or a decrease, and even if caused by non-antigenic substances, *e.g.*, a hypersensitivity to light or drugs. Individual susceptibility may exist to a whole host of substances, such as alkaloids (quinine, atropine), halogen and arsenic compounds (iodoform, salvarsan), salicylates, various vegetable oils, resins, plant pollens, dandruff, hair, feathers, etc. In the case of drugs, Wolff-Eisner suggested that the drug may so alter blood or tissue protein, that it behaves like a foreign protein, a view supported by Landsteiner's experiments (see p. 415). Among the reactions often seen are hay-fever, asthma, and such skin troubles as urticaria (hives), dermatitis. In the case of certain hair dyes (especially the *p*-phenylene diamine series) health department regulations require a "skin-test" should precede actual use.

The term *anaphylaxis* (from *an*, without, *phylaxis*, guarding) should be restricted to those allergies involving hypersensitivity to definitely antigenic substances. A typical illustration would be the following: a small amount of sterile solution containing, say, less than one-millionth of a milligram of crystallized egg albumin is injected into the veins of a guinea pig. After waiting

at least a week (better 10 days or more), about one twentieth of a milligram of the same albumin is similarly injected—and within a few minutes the animal suffers a bronchial spasm causing its death from acute asphyxia. With dogs it is the visceral (splanchnic) area that is most affected; with rabbits, acute dilation of the right heart from spasm of the pulmonary vessels. Men and monkeys are not ordinarily very reactive, and their reactions vary, often being of a cutaneous nature. Non-striated muscle from a sensitized animal will react with strong contractions to very dilute solutions of the specific antigen. The blood of a sensitized animal injected into one of its fellows, gives it a passive sensitization which lasts about a month; apparently the specific precipitins disappear by then, and no others are produced by the unsensitized animals, probably because of absence of the specific catalyst.

The sudden and severe reaction of a sensitized animal to its sensitizing antigen is termed *anaphylactic shock*. An animal which recovers from marked shock of this kind usually will not react again to another “discharging” dose, though sensitivity may be reestablished after a considerable period, apparently through the formation of a new supply of antibodies.

Dr. Auguste Lumière (Lyon, France) found (“L’Anaphylaxie,” Paris, 1926) that a freshly made precipitate of barium sulphate (an insoluble, inert substance) was injected intravenously into a dog, no effect was noticed. If, however, the precipitate was aged so that its constituent particles grew larger and larger, injection was followed by disturbances whose gravity depended upon the size of the flocculates. The older and more aggregated precipitates caused violent shock and death. These effects may be mitigated by getting the animal “accustomed” to the precipitate by repeated small injections, and this fact led Lumière, in common with many others, to consider that the flocculates act by irritating the nerve ends and thus causing spasm. However, others believe that the floccules block the capillaries at certain places (lungs, brain) or are selectively adsorbed at certain areas, thus causing a whole train of disturbances, depending on the locus and the degree of the action. It is thought that certain bacteria (anthrax) and spirillae (*Spirochete pallidum*) act in part by obstructing the circulation.

## DIAGNOSIS

Among diagnostic methods involving colloid chemical principles may be mentioned the Wassermann, Kahn,\* Lange or colloidal gold, colloidal mastic,† and formol tests for syphilis, and the Widal test for typhoid. The differentiation between casts and cylindroids, usually difficult with the microscope, becomes relatively easy in the ultramicroscope or dark field. (See Alexander and Connolly, Science, July 27, 1923.)

## CHEMOTHERAPY AND COLLOID-THERAPY

The initiation of chemotherapy by Paul Ehrlich developed from his observation that when certain dyestuffs were injected into living animals, the dyes were selectively taken up or adsorbed by certain tissues. As far back as 1891 he had noticed that the malarial parasite was strongly stained by methylene blue and could then be differentiated from the cells of the host. This led to the view that dyes or dye-like drugs could be found that would kill the invading organisms but spare the host, and the 606th compound tried against syphilis was Salvarsan (3,3'-diamino-4,4'-dihydroxyarsenobenzene dihydrochloride). Ehrlich, in the course of work with arsenobenzol, defined the Chemotherapeutic Index of a compound as the ratio between the minimum curative dose and the maximum tolerated dose, the result being a fraction. Since individual animals vary in resistance, modern practice is to express the Chemotherapeutic Index by the ratio: Median Lethal Dose/Minimum Curative Dose, which is a whole number. The median lethal dose (L.D. 50) is that dose which will kill 50% of a large group of animals (Trevan, Proc. Roy. Soc., 1927, B, 104, 483).

We will never understand just how many remedies work until we trace their effects on the body colloids—a most formidable task. Many remedies operative *in vivo* do not work *in vitro*.

\* The Kahn test is replacing the Wassermann. See paper by Prof. R. L. Kahn in Vol. II of Alexander's "Colloid Chemistry, Theoretical and Applied." The Lange test uses colloidal gold; see Karl M. Vogel, "The Nature and Interpretation of the Colloidal Gold Reaction," Arch. Int. Med., 1918, 22, 496-516. This includes a detailed method for making the sensitive colloidal gold, by O. I. Lee (Am. J. Med. Sci., 1918, 155, 404).

† See e.g. Adler and Sinek, Klin. Wochschr., 1923, 2, 2071.

All diseases are caused by, or involve, changes in the body colloids which, though delayed by the presence of protective substances, are sometimes irreversible. To cure the disease, we must remove the cause and aid the tissues and body fluids or "humors," as they were called, to return to their normal state of dispersion and swelling. Hippocrates of Cos \* considered that the body was controlled by four humors—blood, yellow bile, black bile, and phlegm. This last may have been the pituitary secretion, now known to exercise a wide control over the endocrine secretion by other glands (see p. 363), for the word *pituitary* means mucus. In a recent book entitled "La Renaissance de la Médecine Humorale," Auguste Lumière (Lyon, 1935), discusses the complicated question of colloidal changes in body fluids.

Bacteria and other invading organisms, as well as the body tissues, have highly specific adsorptive powers, and the "shot-gun" method of try, miss, and try again is our main reliance in finding something that will kill the germ or disease and spare the patient. Quinine, long known and used by South American natives, is still our specific against malaria, a disease which African natives knew was carried by mosquitoes. Speke and Burton (about 1840) commented on the curious superstition of the Congo natives that the sleeping sickness was associated with the appearance of the tsetse-fly. There now have been developed chemical compounds which are said to kill the trypanosome which causes the disease, and is carried by the tsetse-fly.

Many old remedies, relegated to the scrap-heap, had virtues we are beginning to understand, and they are coming into use again. Thus kaolin (clay) is largely being used as a cataplasm and internally as an adsorbent. Some varieties of clay adsorb bacteria and are used therapeutically, *e.g.*, in intestinal diseases like cholera. Charcoal is another colloidal adsorbent in common use; it is sometimes impregnated with drugs which it yields gradually, and it may serve as an antidote by adsorbing strychnine, for example. Freshly precipitated (colloidal) iron hydrox-

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\* In science, as in art, the Greeks acquired much from the Egyptians, whose priests and physicians were highly skilled. The second historical Pharaoh wrote a book on anatomy. Specialists existed in medical practise, and on the walls of the temple at Kom Ombo on the Nile there are pictures of surgical instruments, including a sponge, which so closely resemble modern instruments that their uses are evident.

ide was introduced by Bunsen as an antidote for arsenic; milk, egg white, and other proteins are used for corrosive sublimate poisoning; gruels or other mucilaginous drinks are used against aloes, cantharides, and the like. Dusting powders cool by increasing the free evaporative surface of the skin (Bechhold).

## CHAPTER XXIII

### BIOELECTRICITY \*—MENTALITY

WHAT is called an electrical "dry-battery" is really a wet cell, though its intermediate cylinder of activating fluid containing ammonium chloride is made highly viscous by a gelatinous colloid, *e.g.*, boiled starch. The current flows between the zinc shell and the central carbon electrode which is embedded in a compressed cylinder of carbon and the depolarizing manganese dioxide. The desired quantity (amperage) and intensity (voltage) is built up by suitable assemblage of individual cells. Apart from slow deteriorative internal changes, the activities of dry cells cease when no current is flowing.

In living cells, however, there is a steady "resting potential" which is a consequence of the constant chemical changes incident to cell life (metabolism). Selective adsorption and differential diffusion of ions are factors here, though the case is hardly as simple as that involved in the ideal Donnan equilibrium (see p. 121). The way cells are arranged has much to do with the practical results of their potential gradients. Ordinary nerve and muscle cells are "in parallel," but in the heart muscle the cells form a uniformly conducting cohesive mass or syncytium. While a "dry-battery" tends to reach chemical equilibrium when no current flows, and "runs down" or increases in entropy ("run-downness") when in operation, living cells are continually regenerating by chemical actions on their "food."

Electrical organ cells are essentially modified muscle cells, arranged in series so that their potentials are additive. The electric eel (*Gymnotus electricus*), which sometimes grows as long as 8 feet, has a specially developed organ running nearly the full length of its body, and composed of numerous insulated columns of cells in which the cells themselves are connected in series. The cells have an electromotive force of about 0.05 volt each, so that about 30 gymnotus cells in series give the voltage

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\* I desire to express sincere thanks to Prof. Hudson Hoagland (Clark University) for criticism and suggestions in preparing this section.

of an ordinary "dry battery." \* The total potential difference between the head and tail of the eel may run from 200 to 300 volts, and when released through action of the eel's nervous system, may stun a man or a horse standing in the water near by.

Less than  $\frac{1}{4}$  ampere of current can kill a man, and not more than  $\frac{3}{8}$  to  $\frac{1}{2}$  ampere is used in electrocutions; but the voltage must be sufficient to drive the current through the body, and individuals differ greatly in electrical resistance. Shocks passing through the thorax are particularly apt to prove fatal, in large measure because of their effect on the heart, which is an electrically dominated pump. Alternating currents of several amperes and at high voltages fluctuating several million times per second may, however, be passed safely through the human body, producing only heating effects. In this way artificial fevers may be produced. Such treatments have been efficacious in medicine especially in connection with the cure of general paresis, the tertiary stage in syphilis, and more recently in destroying the germs of gonorrhea. To stimulate living cells, or in extreme cases to produce destruction, currents must flow through them unidirectionally for an appreciable length of time (of the order of milliseconds). Currents fluctuating in direction several million times per second are unable to move ions across protoplasmic membranes and thus produce stimulation.

Considerable clinical use is now made of the *electrocardiograph*, an instrument which records both the rate and the quality of the heartbeat, through the effects produced by the electric currents emitted by the heart as they affect the extremely delicate *Einthoven string galvanometer*. This instrument consists essentially of a gold-coated quartz fiber stretched between the poles of a powerful horse-shoe electromagnet. Trivial currents flowing in the fiber cause it to move in the magnetic field. Recent developments in vacuum tube amplification have made available a variety of less sensitive recording instruments in the study of bioelectricity. The cathode ray oscillograph, devoid of inertia, is one of the most useful instruments in this connection. Another

\* This is the explanation given by biologists. It seems quite possible to the author that electrons may be released upon the coagulation of highly charged cellular colloids by nervous influences, *e.g.*, liberation of a nerve "hormone." Repeated discharges exhaust the organ, and a long period of regeneration is necessary. von Humbolt stated that natives easily take the eel after allowing it to expend its "charge" on horses which they drive into the water.

valuable instrument, when used in conjunction with high amplification, is the iron armature oscillograph, first applied to physiology by Bryan H. C. Matthews (Cambridge University), wherein a sensitive iron armature is made to oscillate as the current in the electromagnet varies. "This instrument can measure potentials as small as a few millionths of a volt, or currents of a few millionths of a millionth of an ampere, and moreover, can measure these when they last for less than a thousandth of a second; with it the minute nerve action potentials, which may be only a few millionths of a volt and last only one or two thousandths of a second, can be accurately measured." (Matthews, "Electricity in Our Bodies," London, 1931.)

Heart cells possess an inherent capacity to undergo rhythmic contraction, which they exhibit even in tissue-cultures. Where a mass of heart cells co-exist, the first one that contracts instantly "fires off" all the others, so that a bit of heart tissue appears to contract as a unit. Microscopic examination shows that there is not always precise synchronism, probably because of local differences in resistance to the exciting electrical wave. The frequency of the heart-beat is dominated by the "*pace-maker*," a small group of cells situated in the sino-auricular node and controlled by both cerebral and sympathetic nerves. The CO<sub>2</sub> tension of the blood, working through certain cells in the medulla, regulates both respiration and heart-beat, increasing them when asphyxia threatens. The very great importance of administering sufficient of the stimulating CO<sub>2</sub> (about 5%) with oxygen in clinical *asphyxia*, has been pointed out by Prof. Yandell Henderson (Yale University).

The nerve terminals are believed to liberate among the heart-cells minute quantities of extremely potent chemical substances (acetylcholine, sympathin).<sup>\*</sup> Certain drugs exert specific action on heart muscle (digitalis, strophanthus, sparteine). If the various blocks of heart-cells do not contract in their proper sequence, the organ ceases to function as a pump, and death quickly follows upon this disorganized, jumbled series of contractions, termed *fibrillation*. This has been demonstrated in tissue-cul-

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<sup>\*</sup> For reviews of properties of these agents see Sir Henry Dale, *Proc. Roy. Soc. Med.* 28, 319; Cannon and Rosenblueth, *Am. J. Physiol.*, 1933, 104, 557-74; Rosenblueth, *Quart. Rev. Biol.*, 1935.



tures, where heart muscle is invaded by proliferating cancer cells. (Prof. Robt. Chambers, N. Y. University.)

The brain is a busy center of electrical impulses, receiving and integrating those from the sensory organs and sending out others over the tiny fibers which are grouped into those relatively large cables we call nerves. Prof. E. H. Adrian (Nobel Laureate, Cambridge University) and his pupils have demonstrated and measured the tiny electrical impulses in nerves (see Adrian, "The Mechanism of Nervous Action," 1932). Each segment of the nerve fiber contributes its own energy as the impulse passes along, so that the process is more like the burning of a train of gunpowder, rather than the passage of a stream of electrons through a wire. But the energy of the nerve segments is promptly regenerated, which is not the case with the powder grains.

The speed of transmission of nervous impulses may reach about 360 feet per second in the larger fibers of mammals; but the speed not only differs with the temperature and kind of animal, but also in the same animal and even in the same nerve trunk. The velocity of conduction is roughly proportional to the diameters of the fibers in a nerve trunk, and these may vary from about  $2\mu$  to  $20\mu$ .

Stronger sensations and more vigorous responses are elicited by greater frequencies of nerve impulses; the number of fibers called into activity and the number of individual impulses per unit of time in each fiber both increase with the strength of the stimulus. But the individual impulses are of uniform amplitude in a given fiber. Thus, when we attempt to lift a cork, the sensory messages received by the brain enable it to send out just such messages as will activate the muscles sufficiently, and no more. Just imagine what would happen to the cork if the muscles made the effort they ordinarily do in lifting a heavy weight. Furthermore, as the flexor muscles contract, the extensor muscles must relax, and *vice versa*.

The brain automatically keeps sending out impulses to our muscles to keep us standing upright. Merely standing still involves considerable involuntary "exercise," which is reflected in increased activity of heart and lungs. Therefore in the "rest cure" for pulmonary tuberculosis, where the lungs are to be immobilized as far as possible, the patient is not permitted even

to stand, but must recline in a relaxed position. When unconsciousness supervenes, as in fainting, the muscles relax and the person falls limply.

There is a logarithmic relation between the strength of the stimulus and the impulse frequency per single nerve fiber unit (Matthews). According to experiments of Prof. Hudson Hoagland (Clark University), certain sensory units and their attached nerve fibers appear to come into play according to the distribution curves of their thresholds of activation (J. Gen. Psych. 1927, 3, 351-73). This gives a basis for the Weber-Fechner law correlating psychological sensation with strength of stimulus.

The human cerebral cortex gives out electrical oscillations, which have been picked up through the skull and seem to be of a "spontaneous" nature. Three types of these rhythmic electric potentials have been distinguished by Dr. A. L. Loomis (Tuxedo, N. Y.), Prof. E. N. Harvey (Princeton University) and G. Hobart (Science, 1935, 82, 198; 1936, 83, 239):

- (1) *Trains*, lasting 1 to 30 seconds, with a frequency of about 10 per second. First observed by Berger (Arch. f. Psychiat. u. Neur., 1929-35), and termed the "*Berger rhythm*" by Adrian (Adrian and Matthews, "Brain," 1934, 57, 355).
- (2) *Spindles*, lasting less than one second, with a frequency of about 14 per second. Less numerous than trains, and appearing only during deep sleep.
- (3) *Random*, of variable frequency, appearing irregularly during sleep.

Mental concentration or emotion stops the output of trains, sometimes from only part of the head. Opening the eyes stops the trains if the room is not completely dark, and the same effect is produced by a feeble flash of light in a dark room.

When a person is falling asleep, the trains, after persisting for a while, pass over into random impulses. Any *unusual* sound (cough, whisper, faint footstep, rustling of paper) generally results in a prompt reappearance of trains, although louder *usual* noises (automobile horn) or even a bright light may not have this effect. Loomis and his collaborators "are inclined to believe that this starting of trains by sound is not a direct result of the

sound stimulus but is connected with a change in the general level of brain activity."

Hoagland has also produced evidence ("Science," 1936, 83, 84-5) indicating that rhythmic activity in the central nervous system (*e.g.*, the Berger rhythm from the occipital cortex in man) arises as relaxation oscillations at frequencies directly proportional to underlying respiratory (oxidative) changes taking place in the cells of the cortex. He has furthermore shown that the frequency of other types of rhythmic activity (*e.g.*, counting seconds, or tapping out regular intervals) also appears to depend directly upon the speed of similar underlying chemical events. "Measurements of the estimations of short durations indicate the existence of a master chemical clock of a specific nature, possibly the slowest of the series of irreversible processes involved in the respiration of certain parts of the brain." (J. Gen. Psychology, 1933, 9, 267-87; see also "Pacemakers in Relation to Aspects of Behavior," Macmillan, 1935).

It has been suggested that since nerve conduction is relatively slow in cold-blooded animals (say 40 feet per second on a cold day), a relatively small, or a warm-blooded, aggressor might have bitten the tail of a huge brontosaurus (total length, about 120 feet) and been able to jump away even before the brontosaurus could have felt the bite and moved his tail out of danger. But experiment shows that our nervous system causes us to pull away a burned finger automatically before we actually feel the burn, and Prof. C. S. Sherrington (Nobel Laureate, Oxford University) showed that animals whose spinal cords have been transected still show flexion reflexes. Crocodiles move their tails with a very short latency, when touched, and the brontosaurus may have had a sacral plexus or "hind brain." \*

The establishment of a thermostatic, neuromuscular system controlling heat loss so that an animal became "warm-blooded," was an important evolutionary advance. One factor involved in the advance seems to have been the separation of venous from arterial blood by changes in the structure of the heart. The crocodile represents an intermediate stage, only a partial separation of venous and arterial blood occurring in this animal.

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\* In this connection see the verses entitled "Intellectual Giants of Antiquity," Ind. Eng. Chem., News Edition, 1931, 9, 359.

## THE NERVOUS SYSTEM \*

The major portion of the nerve cells in the human body are in the brain and the spinal cord, protected from injury by a bony sheath. What we term "nerves" are simply long fibers (axons) which grow out from nerve cells, somewhat like "feelers" from the nose of a cat. Prof. C. C. Speidel (University of Virginia) has watched the process of growth in the tails of tadpoles, and recorded his observations in motion-picture films (see *Am. J. Anat.*, 1933, 52, 1-75; *J. Compar. Neur.*, 1935, 61, 1-62). A pioneer "growth cone" worms its way through certain tissues at an average rate of less than 1  $\mu$  per minute, spinning behind it a nerve fiber along which glide subsequent growth cones. Roving cells (fibroblasts) tend to collect only about those fibers which have emerged *from myelin-containing* areas, and tend to form primitive sheath cells which later elaborate myelin sheaths for the fibers. This is consonant with the view that particles of myelin act as specific modifiers for the cellular catalysts. (See p. 375.)

While nerve cells tend to restore broken connections by the extension of existing fibers or the outgrowth of new ones, they do not regenerate when severely injured, nor are they replaced by other cells. The loss of a nerve cell is final and irreplaceable; but surviving cells may take over its functions to a greater or less extent.

Chemically, brain and nervous tissue consist mainly of hydrated lipid colloids, *e.g.*, cephalin, myelins, lecithin, and cholesterol, which latter is believed to help maintain the proper water balance or turgidity. Prof. Martin H. Fischer (University of Cincinnati) states that a swelling of the brain amounting to 5 per cent. causes coma, while 8 per cent. causes death. Drs. S. DeWitt Ludlum, A. E. Taft, and R. L. Nugent (*Arch. Neur. and Psychiat.*, 1930, 23, 1121-37) have demonstrated by ultramicroscopic examination the colloidal nature of unstained nervous tissue elements, and their changes under various conditions. The intercellular substance in brain appeared "like boiled farina"—a finely granular, somewhat tenacious substance—eminently suitable for a support or packing for the nerve elements which it surrounds.

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\* Naturally, no attempt is made here to give a detailed description of the highly complicated nervous system, for which reference must be made to special treatises.

This gray supporting substance is most abundant about the cells, and less abundant about the nerve fibers in the brain. Apparently it bears the same hydrating relation to brain cells, as does connective tissue to other cells, *e.g.*, muscle, governing their turgidity and cooperating with the capillary circulation.

### PSYCHIATRY \*

The proper functioning of the brain and the nerves depends largely upon the maintenance of their constituent colloids within certain limits of swelling and dispersion (see p. 405). However, interference with the normal catalytic behavior of the cells by modifiers (p. 375), by elutors (which can remove modifiers), by lipoid-soluble substances (*e.g.*, chloroform, ether), or by enzyme inhibitors of any kind, may also be an important factor. *Chemism as well as colloidalilty must be considered*, and the balance between normality and abnormality is a narrow one. As Dryden wrote (Absalom and Achitophel) :

"Great wits are sure to madness near allied,  
And thin partitions do their bounds divide."

Prof. S. D. Ludlum (University of Pennsylvania) and his collaborators have adduced evidence indicating that in the toxic delirious state of acute mental disease, the blood serum, as measured by physico-chemical methods, shows a high specific gravity, high viscosity, high total protein, with an increase in globulin and a diminution in free water. This condition is correlated with the sympathetic side of the autonomic system ("involuntary" nervous system). On the other hand, in the asthenic (or depressed) and other non-reactive states, there is low protein, lowered globulin fraction, and an increase in free water. This state is correlated with vagus (pneumogastric) nerve preponderance in the autonomic system. Such blood, with low specific gravity and viscosity and increased free water, tends to permeate the

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\* Thanks are due to Dr. Ludlum for some information in the preparation of this resumé, and for advice on other matters. In 1926, shortly after the publication of Vol. I of "Colloid Chemistry, Theoretical and Applied" (Chemical Catalog Co.), Dr. Ludlum pointed out to me that the concluding paragraph of the first chapter (here quoted on p. 37) checked with much of his experimental data (see paper by S. D. Ludlum and A. E. Taft in Alexander's "Colloid Chemistry," Vol. III 1928). Also "The Problem of Mental Disorder," Nat. Research Council, McGraw-Hill, 1934.

intercellular substance of the brain and to cause or permit swelling. The question of the turgescence of the brain would therefore seem to depend upon the circulatory pressure in the capillaries and the colloid osmotic (oncotic) pressure of the serum colloids, which latter depends upon how near the blood serum lies to the condition of optimum colloidalilty. (See p. 398 and p. 400.)

Sir Joseph Barcroft (Cambridge, Nobel Laureate) in his Terry Lectures at Yale University, Oct., 1936, classes the effects of physico-chemical unbalance under two headings: "depression complex," characterized by weakness, inertia, coma; "excitement complex," characterized by irritability, delerium, convulsions.

All kinds of degrees and localizations can naturally exist in these deviations from normality, and the underlying causes may be various—disturbance of the delicate capillary circulation by drugs, by locally adsorbed products of infections, intestinal stasis, etc., by hormones released in the body as a result of undue or unbalanced nervous excitement. Thus Dr. George W. Crile (Western Reserve University) bound a rabbit with tape so that it could not move, and allowed a tethered dog to bark at it. The rabbit died of "fright" and its brain showed extreme congestion, probably associated with excessive release of hormones (*e.g.*, adrenalin) without the possibility of any corresponding motor activity to act as a natural release or relief valve to the greatly enhanced blood pressure. The blood supply throughout the body is under nervous control, to some extent directly, to some extent indirectly through the endocrine glands which, by nervous stimulation, pour their powerfully acting secretions (hormones) into the blood stream.

When the psychiatrist says that a neurosis has become a psychosis, he is only recognizing a clinical fact without even hinting at the underlying causes. Broadly speaking, in many mental disorders there is a preliminary *reversible* stage, which, if not taken in time, may lead to later stages which are partially or totally irreversible. Since the physico-chemical changes of many of the biocolloids (*e.g.*, gelatin and albumin) are at first reversible but may become practically irreversible as the coagulative or alterative changes persist or increase (see p. 301 on denaturation), it is natural to inquire whether many forms of insanity do not represent acute diseases, amenable to treatment before the damage to irreplaceable nerve cells has become irreversible.

Once this has come to pass, what is treated is an incurable wreck. Even progressive forms of insanity or nervous disease might be more successfully treated if we only understood and could control the inexorable physico-chemical changes. For example, patients with dementia praecox become rational for a while following treatment with CO<sub>2</sub> and O.

Dr. A. Justchenko ("The Nature of Mental Diseases," Dresden, 1914) states that the viscosity of the blood is usually increased in dementia praecox, senility, and manic-depressive insanities, especially during the periods of excitement. Auguste Lumière found that the blood of an epileptic, taken just before a seizure and injected into a rabbit, produced epileptiform convulsions in the animal. The active part of the serum settled out on standing and could also be separated by centrifugation, indicating that it is a flocculate of some sort.

Bancroft \* and Richter (Proc. Nat. Acad. Sci., 1930, 16, 573; J. Phys. Chem., 1931, 35, 215), working with yeast cells, confirmed the view expressed in 1870 by Claude Bernard that anesthesia involves a reversible agglomeration of certain colloids in the brain. Recently, Makarov (Protoplasma, 1935, 24, 593) independently concluded that "the action of narcotics, in the broad sense of the term, on protozoa is to cause a decrease in dispersion of the colloidal material in the cells." Recent experiments by Bancroft, Heming and Rutzler at Cornell University show that anesthesia of clothes-moth and *Sciara* larvae involves a reversible agglomeration of proteins which can be seen and photographed. A series of papers from the same laboratory indicate that a like process is observable in morphinism, alcoholism, strychnine and histamine poisoning, the action of bulbo-capnine, and such functional mental disturbances as the manic depressive and dementia praecox paranoid psychoses, functional insomnia, and insomnia due to caffeine. Dementia praecox, catatonic and hebephrenic, as well as the toxic psychosis produced by over-dosage of sodium rhodanate, also involve an *over-dispersion* of protein colloids.

On the other hand, preliminary, unpublished experiments indicate that reversible *over-agglomeration* of protein colloids accompany nervous exhaustion, neuritis, sciatica, hypertension

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\* The next three paragraphs are condensed from a memorandum kindly supplied me by Prof. Wilder D. Bancroft, (Cornell University).

due to nervousness, and certain cases of hay fever, arthritis, and stammering. Similar, though less far-reaching results were obtained by Pauli thirty years ago (Pauli: "Physical Chemistry in the Service of Medicine" (1906), pp. 81, 87; Bancroft and Rutzler: Proc. Nat. Acad. Sci., 1934, 20, 508).

According to Bancroft, the experimental evidence indicates that a suitable dosage of sodium rhodanate (a very pure sodium thiocyanate and a satisfactory peptizing agent for proteins), will counteract the craving of any drug addict or alcoholic following upon withdrawal of the causative drug, provided there is no medical contra-indication and provided also that the patient gives complete cooperation. The permanence of the "cure" depends on the degree of cooperation. "Sodium rhodanate has been used successfully on either man or animals or both to counteract all of those conditions which have been shown to be due to or accompanied by reversible agglomeration of protein colloids." According to Ivy (Ivy *et al.*: J. Infect. Dis., 1934, 55, 112) and Mitchell and Goltman (J. Pediatrics, 1935, 6, 57) sodium rhodanate tends to counteract bacillary dysentery (Shiga type), a disease which clearly seems to be accompanied by reversible agglomeration of protein colloids. Bancroft, Farnham and Rutzler ("Science," 1935, 81, 152) "believe that a regular dosage of this compound for normal people over forty-five years will increase the probable expectancy of life by at least two years."

Prof. Bancroft states: "The medical men do not accept these conclusions."

Changes which accompany a disease cannot safely be assumed to be the cause. In view of the extreme complexity of organization of the animal body, and even of every cell and tissue within it, many aspects of diseases other than changes in protein dispersion, must be considered if we would envisage the entire disease process. Different animals and even different individuals may react quite differently to the same chemical substance. The human infant does not tolerate morphine, but may withstand atropine better than an adult.

### CONSCIOUSNESS AND MENTALITY

Normal consciousness seems to be based upon a certain zone of chemical reaction rates in the brain, which is dominated by



the cellular colloids, including their catalysts. Too rapid a rate as well as too slow a rate leads to unbalance, as is the case with the projection of motion pictures. In a highly complicated series of interrelated chemical reactions, the velocity of the whole process is controlled by that of the slowest reaction of the series, just as the speed of a fleet is that of the slowest ship. And the control may pass from one reaction to another, if the slowest reaction speeds up or a more rapid reaction slows down for any reason.

Prof. Hudson Hoagland (*lib. cit.*, p. 3) takes the behaviorists to task for obscuring certain important problems by shifting attention away from behavioral mechanisms with roots in the natural sciences, and going over to "verbal constructions either deduced from, or induced by, the experimental data. . . . This oversimplification of reflex physiology, as is clear from the writings of Sherrington's laboratory, is not due to the principal investigators of reflex phenomena. It seems rather to have grown up as a by-product of the faith of the behaviorists in stimulus-response empiricism, coupled with their desire for physiologically simple interpretations." (See also p. 10 and the Preface to Vol. II (Biology and Medicine) of Alexander's "Colloid Chemistry" (1928).)

Depth of mental focus is what is now most needed by the physiologist, the biologist, and the physician, as a prerequisite to their best work; for they are dealing with exceedingly complicated systems, where increasing complexity enormously magnifies the number of possible structures and relations. Below the intricacy of organization which the microscope reveals even in a single cell, lie the bewildering phenomena of the colloidal zone, of molecular orientation and aggregation, of atomic groupings to form molecules, and of sub-atomic units to form atoms. These are not isolated happenings, but are interrelated parts of every phenomenon and serve to make the whole. No single instrumental score constitutes a symphony, even though it may carry the main theme most of the time. The whole orchestra expresses the music, of which the layered score is the written record.

Out of the inconceivably great number of possibilities in life processes, the relatively few that regularly develop are forthcoming because they are made vastly more probable by factors which reach down to the very electronic configurations of atoms

themselves. Every chemical, physical, biological, or physiological change follows as a consequence of the shifting about of material particles—in final analysis, all we do experimentally is to change the position of matter or of material particles, and follow the results of the play of natural forces. In biological and medical phenomena, the units whose behavior we strive to follow are very complex and are themselves undergoing continuous changes. It is often difficult if not impossible to form a precise mechanical picture of what goes on. No simple explanation, formula, or group of formulas, will ever give us an understanding of the behavior of even a single amoeba. *Few phenomena are as simple as are the scientific theories advanced to explain them.* Dr. N. Rashevsky (J. Gen. Psychol., 1931, 5, 207 and 368) has considered learning mathematically as a property of physical systems, and discussed possible brain mechanisms and their physical models. He points out that the view that learning is a particular type of hysteresis (see p. 149) is not a new one, having been proposed by T. B. Robertson (Arch. int. Physiol., 1908, 6, 388). Rashevsky states that if we give the term hysteresis its most general meaning, "the dependence of the properties and behavior of a physical system not only on the instantaneous environmental conditions, but on all the previous history," we are simply giving a description of learning (and in fact all mental phenomena) in physical terms when we class them as special cases of hysteresis. He distinguishes between time-lag hysteresis which vanishes with time, and hysteresis due to the existence of multiple equilibria which does not vanish with time. The functioning of robots or "mechanical men" commonly depends upon delayed reactions allied to hysteresis.

But even though we may distinguish the various chemical and physical changes which seem to be essential to brain function, just how these become *consciousness*, *thought*, and *reason* still remains the mystery expressed in the old philosophical circle: "*What is mind?*" "No matter." "*What is matter?*" "Never mind." "*What is spirit?*" "It is immaterial."

The late Prof. Leonard B. Troland (Harvard University) in a series of books on Psycho-physiology (D. Van Nostrand Co., 1929-32), made a notable attempt to correlate a wide range of chemical, physical, and physiological knowledge with the live views of various schools of psychology. His untimely and much

lamented death prevented the publication of the fourth and final volume of this series, which was to have been on "The Ultimate Theory of Mind and Matter." In the Preface to the third volume on "Cerebration and Action," Troland pointed out that the *Behaviorists* are concentrating on a single aspect of the psycho-physiological problem, *i.e.*, response, regarded, as a physiological mechanism. And those who adhere to the so-called *Gestalt* school of psychology are concerned almost exclusively with cerebration, using consciousness and behavior as instruments for studying cerebration. On the other hand, classical psychology has dealt mainly with consciousness, *per se*, but has utilized sensory relationships almost exclusively to study its psychophysiological dependencies. A comprehensive account must include *all* facts and aspects, and Troland thinks we must be courageous enough to envisage the entire system. (See also Troland's earlier book, "Mystery of Mind," Van Nostrand Co., 1926.)

Matter fluctuates—relations persist. Our material bodies are undergoing continuous chemical change, with new atoms and molecules replacing old ones; in fact, experiments with the new "heavy hydrogen" (atomic weight, 2) indicate that even in some "stable" compounds there is quite some shifting about of atoms. But the *forms* and the *form-determiners* remain much more stable, although they, too, may undergo gradual alteration with growth and age.

"Relations," divorced from physical units, become purely metaphysical. We must envisage the reality of physical units (even if their ultimate nature eludes us), and the reality of mental and psychic phenomena, even if we cannot understand how physical changes become translated into consciousness and thought. The exposition of a perfect system of material concomitants to mentality fails to bridge the chasm between mind and matter. To say that mind is *in* matter (panpsychism) simply combines into one the age-old mystery so beautifully expressed by the Persian poet, Omar Khayyam (*e.g.*, Rubaiyat 31-34). But here physics ceases and metaphysics begins.

Robert G. Ingersoll once wrote: "Our ignorance is God; what we know is Science." But with the gradual increase in our knowledge, we are brought more and more into contact with the enigmas of the unknown, which Ingersoll termed God. *As we extend the frontiers of our knowledge, we correspondingly extend the frontiers of our ignorance.*

CHAPTER XXIV  
EXPERIMENTAL SUGGESTIONS  
OR  
LABORATORY MANUAL \*

I. PREPARATION OF COLLOIDAL DISPERSIONS

*A. Aggregation Methods*

1. CAUSING aggregation of dissolved substances by decreasing solubility.

(a) Tincture of green soap (alcoholic solution) is a clear transparent true solution of potash soap (mainly oleate). Stir a teaspoonful into a glass of water and note that there is at once produced a hazy colloidal solution, whose particles show active Brownian motion in the microscope or ultramicroscope. Evaporate off the water in a double jacketed pot and then note that on adding a glass of water to the residue, it again returns to colloidal solution, showing that the soap is a *reversible colloid*.

(b) Try a similar experiment with an alcoholic solution of gum mastic (or shellac). The gum forms a colloidal dispersion when some of its alcoholic solution is dropped into water, but when dried out, the residue will *not* redisperse in water (*irreversible colloid*).

(c) Try a similar experiment with a perfume extract (alcoholic true solution of essential oils). The colloiddally dispersed particles of the essential oils are liquid and we get an *emulsion*. On evaporation of the water, the more volatile portions of the oils go off with it; but the residual oil will (in general) not re-emulsify.

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\* These simple *qualitative* experiments are meant for the general reader or the novice, and they are based on materials and apparatus generally available or easily obtainable. For more extensive quantitative experiments, specialized books or the instructor must be consulted. However, as Prof. P. P. von Weimarn has pointed out, qualitative experiments may often be made roughly quantitative by carefully observing and varying quantities and conditions.

2. Causing aggregation of molecularly dispersed substances, by chemical change.

(a) Into a cup of *boiling hot* water pour a few drops of ferric chloride solution (or tincture of chloride of iron, which is an alcoholic solution). The iron salt hydrolyzes, giving a rich brown colloidal solution of ferric hydroxide, and dilute hydrochloric acid. If most of the acid is dialyzed off, the colloidal solution will be quite stable (see U. S. Pharmacopeia for preparation of "ferri hyd. dialysat."). If the acid is allowed to remain, it produces a gradual flocculation of the iron oxide hydrosol. Compare its color with that of the same amount of iron solution mixed into a cup of *cold* water. This hydrosol may be stable though free from detectable traces of chlorine, thus disposing of the fallacious assertion that chlorine or hydrochloric acid are *essential* for its stabilization.\*

(b) Put a few good sized pinches (say  $\frac{1}{4}$  gram) of ammonium vanadate in a cup and drop on it about 10-12 drops of strong hydrochloric acid. The dark red-brown vanadic acid ( $V_2O_5$ ) gel that forms is mixed with the ammonium chloride incidently produced. If this latter be dialyzed off (for details see p. 447), the pentoxide will form a dark brown fluid hydrosol, which may be diluted with distilled water without causing coagulation. If the diluted hydrosol be allowed to *age* for a few weeks (in a stoppered bottle to prevent evaporation), it will show, when dilute, a *streaky* appearance on being shaken or stirred. On ageing, rod-shaped aggregates are formed which are oriented *at random* when the fluid is at rest, but which point in the direction of flow when the liquid moves, just as logs floating in a stream tend to point end-on to the current, though in a still lake they would point any which way.

(c) Make a little gold chloride as follows: (1) Dissolve a little of the metal off from an old piece of gold jewelry by attaching it to a cotton thread and dipping it for a while into aqua regia (3 parts strong hydrochloric acid, 1 part strong nitric acid.) (2) Put a strip of zinc in the metal solution; the dissolved gold

\* For details see C. Harvey Sorum, J. Am. Chem. Soc., 1928, 50, 1263. Freundlich and Wossressensky (Kolloid Z. 1923, 33, 222) also prepared stable electrolyte-free ferric hydroxide hydrosol by reducing iron carbonyl with hydrogen peroxide. P. A. Thiessen and Otto Koerner (Z. anorg. und allgem. Chemie 1929, 180, 115) have also produced stable but sensitive electrolyte-free iron oxide hydrosols from iron ethylate.

and copper will precipitate out on the zinc as a black "mud." (3) Dissolve the copper from this mud with dilute sulphuric acid, which will leave the gold. (4) Dissolve the remaining black gold "mud" (after washing it) in as little aqua regia as possible, allow to evaporate to dryness, and dissolve in distilled water. This should give a bright yellow solution of chloride of gold,  $\text{AuCl}_3$ .

Let us now treat the chloride of gold so as to separate the chlorine from the gold. The liberated gold will *tend* to aggregate into particles large enough to settle out again as a black mud. We oppose this tendency either by using high dilution, by avoiding the presence of coagulating electrolytes, or by employing protective colloids.

*Faraday's method.* Stir 10-20 drops of the gold chloride solution into a carefully cleansed cup of distilled water, and then add about 10 drops of a solution of yellow phosphorus in ether.\* A brownish or orange tint should slowly develop, gradually becoming ruby-red as the gold particles become larger. If the water is not sufficiently pure, further aggregation may occur, the solution becoming purplish, then blue or blackish, and depositing its gold. If a stable red hydrosol is not obtained, repeat the experiment, adding a little gelatin or gum arabic solution *before* adding the phosphorus solution.

*Zsigmondy's method.* To the diluted gold solution, add a drop or two of potassium carbonate solution. Warm the gold solution, and then add a few drops of formaldehyde to reduce the gold. If a protector is needed, use gum arabic, because formaldehyde combines with gelatin.

*Wo. Ostwald's method.* Warm the gold solution and add a few drops of a solution of tannic acid, which not only reduces the gold, but also serves as a protective colloid. If no tannic acid is available, a little may be dissolved out of a piece of *washed* sole leather by ammonia, and the ammonia boiled off.

## B. Dispersion Methods

1. *Mechanical.* Put a small lump of clay in a mortar; add enough water to make a thin cream, and grind, and *grind, and*

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\*This is poisonous and dangerous to unskilled persons. If necessary, have some experienced person do it for you.

*grind*. It will greatly help to add a little gelatin, gum arabic, or tannic acid dissolved in *weak* ammonia. Mix the thoroughly ground mass into a quart of distilled water, and allow to stand a few days. Depending on circumstances, more or less of the clay will still be afloat as a colloidal suspension, the balance having settled out.

2. *Deflocculation*. Put about  $\frac{1}{4}$  teaspoonful of lamp black (or carbon black) into a warm  $\frac{1}{2}\%$  soap solution and shake well. The carbon particles should be separated and form a stable black dispersion. Try the same experiment, using zinc oxide and 1% gelatin solution.

3. *Emulsions*. Make mayonnaise according to any of the good cook book recipes. Or shake up a teaspoonful of olive oil in a warm  $\frac{1}{2}\%$  soap solution.

4. *Spontaneous dispersion*. ("Natural" colloids.)

(a) Stir gum arabic in cold water; a colloidal solution results.

(b) Soak a bit of gelatin or glue in cold water until it is soft (powdered gelatin softens immediately). Then warm. A colloidal solution is obtained, which, on chilling, will set to a jelly if sufficiently concentrated.

(c) Stir a little starch in cold water and note that it quickly settles out on standing. Stir it up again and heat to burst the starch grains; a paste or sol results, depending on concentration.

(d) Milk contains salts and sugar in crystalloidal solution; casein, etc., in colloidal dispersion; and fat in emulsion. The cream layer that rises consists of a dispersion of fat in an aqueous medium, and will *wet* blotting paper. When beaten to butter, we get a dispersion of water in fat, which *greases* blotting paper. Put some butter in a frying pan and fry out the water from it—note how it splutters until all the water is gone.

## II. OPTICAL EFFECTS

*Faraday-Tyndall Effect*. Add a little of any of the colloidal solutions made as described under I, to a glass of distilled water, put the glass in a darkened room or in front of a black cloth, and then allow a narrow beam of sunlight (or bright electric light) from a small hole or slit in a piece of metal or cardboard, to pass through the glass. Examine the beam, looking at right-angles to its course. The beam becomes visible because the tiny particles in it diffract or scatter the passing light.

Similarly, a searchlight cuts a "path" through hazy or foggy air at night, and in a sunbeam, especially against a dark background, we see the otherwise invisible motes. A magic lantern or projector shows the same phenomenon; tobacco smoke, mica dust, or other fine powders may be used to make the air hazy. Apply the light beam to the aged vanadium pentoxide sol (page 443) and note the peculiar silky streaked effect of the orientation of the rod-shaped particles.

Note the color changes evinced as substances change in degree of dispersity—gold passes from bright yellow, through orange, ruby red, purple and violet, to black, as the particles grow larger. Very fine particles tend to scatter the shortest waves of light (blue); therefore very dilute milk, looks "blue." The longer red waves are not so readily scattered. Therefore sunset colors generally transmitted are reds, oranges, and yellows (the blue being scattered out); and red danger lights are visible further in hazy air than blue lights.

### III. DIFFUSION, DIALYSIS, FILTRATION, ULTRAFILTRATION

*Diffusion.* Put drops of various colloidal solutions, and also of red ink (eosine) and violet ink (methyl violet) on a piece of clean white blotting paper, and see that in some cases the dispersed material will diffuse to the outside of the drop with the water, which, as a rule, soon outruns the colloid material, and makes a colorless "water" ring beyond it. The reverse side of the blotter generally differs from the obverse (see J. Alexander, J. Am. Chem. Soc., 1917, 39, 84-8). Concentration of the coloring material is important, for it may clog the pores of the paper almost immediately and thus form a barrier to diffusion. With ferric hydroxide sol and India ink, the colloid material hardly diffuses at all, and the clear water ring is larger. Try solutions of various Easter egg, and other "dyes." Also milk and cream.

Mix several different dyes, or mix dyes with ultramarine blue and India ink, and then drop the mixtures on a clean white blotter. Note that some dispersed substances diffuse further and faster than others, thus causing separation by *differential diffusion*.

*Patriotic Test-tube.* Make the patriotic test-tube experiment described on page 118. The phenolphthalein may be obtained from the druggist, or from one of the common laxatives which contain it.



However, a good substitute indicator can be made from ordinary red-cabbage, by boiling some leaves to extract the purplish coloring matter. Vinegar (acid) turns it bright red; lye (alkali) turns it bright blue; and ammonia turns it green. If the agar solution be made up with red-cabbage water, the whole tube will, originally, be purplish, and the acid band will show red instead of white, the Prussian blue band being the top one, as before, but slightly modified in shade by the cabbage-water color.

*Dialysis.* Dialyzing thimbles may be bought, or may be made thus: pour some collodion into a large test-tube or a small flask or glass, roll it about so as to cover the entire interior and pour off the excess. After allowing the collodion to "set" for say half a minute, carefully pour in cold water, and when the collodion film has become tough, remove it from the glass. Introducing a little water between the glass and the film, at the mouth of the vessel, is a great help. (*Collodion solvents are inflammable!*)

Put a mixture of gum arabic and salt solution in the dialyzing thimble, close its neck with a rubber band, and then hang it into running water, or into water which is frequently changed. Taste will readily show that the salt passes through into the outer water, while the gum which remains behind, becomes less salty. To prove that the gum is mostly left behind, evaporate the contents of the thimble and recover the gum.

Another simple way to make an efficient dialyzer is to place a folded filter paper in a funnel (the filter paper should project above the edge of the funnel), pour collodion into the filter paper so as to coat it thoroughly, drain off the excess collodion, and then allow water to flow upward through the funnel tube from a rubber hose attached to the cold water tap. When the collodion film has set, wet its upper surface with cold water, and drain off. Then place the mixture to be dialyzed in the filter paper, and open the tap slightly, so that a continuous supply of fresh cold water flows up through the funnel tube and laves the under side of the collodionized filter paper.

Colloids may be freed from diffusible impurities (salts, acids, alkalies, etc.) by dialysis. Often some of the colloid itself is lost, for many colloids diffuse perceptibly. The more concentrated the collodion solution, the "tighter" or more resistant to diffusion the dialyzer will be.

Instead of using collodion, a warm weak ( $\frac{1}{2}$  to 2%) gelatin solution may be poured into the filter paper in the funnel, the excess drained off and replaced by a 5% solution of formalin. Let this soak in for about 1 hour to harden the gelatin and render it partially insoluble.\*

*Filtration.* Add hydrochloric acid to a solution of silver nitrate. Note that the white precipitate of silver chloride readily settles out on standing, and will not pass through an ordinary filter paper. Repeat the experiment, adding some gelatin or gum arabic solution to the silver nitrate *before* addition of the acid. Note that the precipitate of silver chloride does not settle out and will readily pass through the same kind of filter paper.

*Ultrafiltration.* Where diaphragms are sufficiently close or "tight" to prevent, largely or completely, the passage of a certain colloid by filtration, the fluid medium and even the colloid itself may be *forced* through by application of pressure. Generally, simple apparatus is not possible; but the principle may be demonstrated by attaching *one end* of a rubber balloon with double outlets (*e.g.*, obtained from a toy "bagpipes") to a dialyzing thimble; and blowing the balloon up, securing *the other end* to maintain the pressure. A glass tube over which has been slipped a piece of rubber tubing, makes a good connection between the balloon and the thimble, and can be tied air-tight.

#### IV. SURFACE TENSION, VISCOSITY, SWELLING

*Surface Tension.* (1) Dip a brush with long, soft hairs (camels' hair brush) into water and note that the hairs tend to float free of each other. Now withdraw the brush, and notice that the drawing together of the water-films between the hairs, pulls the hairs tightly together (W. D. Harkins).

(2) Float a small drop of fat, butter, or olive oil on the surface of hot water. The surface tension of the droplet tends to form a sphere, but this is flattened out by gravity into a lens-shaped drop. (A mercury droplet on a glass plate is nearly spherical, owing to the high surface tension of mercury.)

Now add to the water some lye solution (caustic soda), and note that the fat droplet breaks up into a fine emulsion. The main factor here is the formation of some *soap*, by the action of

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\* Formalin (40% formaldehyde) is poisonous, and will harden the skin.

the alkali on the fat or on its free fatty acid (usually present); and this soap *lowers* the surface tension at the interface between the fat and the water (F. G. Donnan). Emulsification can, therefore, also be produced by adding a little strong soap solution, instead of adding the lye. Slight agitation may be essential to effect emulsification.

*Spreading.* Dust a little talcum or other light powder on the surface of a glass *full* of water, and touch the corner of a bit of soap into the center of the surface of the water. The soap instantly spreads over the water as a superficial film, and drives the floating powder to the rim of the glass. Oleic acid and camphor will act in the same manner as does the soap. These surface films are only *a few*, and often only *one* molecule deep. If enough of the film-forming molecules are present and they are long and *polar* (i.e., show greater attraction to air at one end and to water at the other), the molecules may pack together like logs floating end up. With fewer molecules, they may float lengthwise in the water and may leave bare gaps. Make experiments using large vessels (dishpans, etc.) and smaller and smaller amounts of soap, camphor, etc. The area over which they spread is shown by the talc, and can be measured and compared with the amount of spreading agent used (I. Langmuir).

Soak some match-sticks or toothpicks in soap solution and then dry them out. On floating the soaped sticks on water, note how they float *apart*. Now add some acid (vinegar, hydrochloric acid) and see how the sticks approach and cling together.

*Surface Orientation of Molecules.* Put a piece of pure stearic acid (or other pure solid fatty acid) about the size of a pea, on the surface of a cup of *hot* water. The fatty acid should melt to form a lens-shaped drop, which solidifies again as the water cools. When the fatty acid is thoroughly hard, remove it and dry carefully without disturbing the surface—or allow it to stand in a cool place until it dries spontaneously.

Note that the bottom of the lens which has solidified *in contact with water*, can be wet by water; whereas the upper surface of the lens, which has solidified *in contact with air*, repels water. The “oily” ends of the molecules of fatty acid are directed outward in the upper surface, whereas the “water-loving” or hydrophile ends are directed outward in the bottom surface of the lens of fatty acid (Devaux).

*Capillary Rise.* If a clean glass tube with a very small, hair-like (capillary) bore is dipped into clean water, the water rises in the tube, due to the surface attraction between the glass and the water (*wetting*). The *height* to which the water rises, depends upon the *strength* of its film at the glass surface, that is, upon its surface tension, because gravity tends to drag the water down, and the strength of the film must just balance the gravitational pull on the column of water.

A bit of broken thermometer tube, open at both ends is good to use, as it is graduated, and you can see the effect of adding soap, lye, acid, etc., to the water. See how far alcohol will rise. A medicine dropper with a long thin point and the rubber bulb removed, will show capillary rise to a slight extent.

*Stalagmometer* or "*Drop-measurer*."—Use an ordinary medicine dropper or a pipette, and count *how many drops* you get from the *same volume* of different liquids, *e.g.*, alcohol, having a lower surface tension, gives *more drops* than water, because the drops tear loose more readily, despite the fact that water has a much greater weight for the same volume of drop. Try pure water and then soap-water. Soap lowers the surface tension of water against air, and we get more drops.

*Viscosity.* Soak the *same* amount of gelatin in *different* amounts of cold water, and when softened, dissolve by warming. Note how much "thicker" or viscous the more concentrated solutions are than the more dilute ones. Watch the solutions as they cool, and note how the viscosity of each solution increases as it cools, and finally jells if the solution is sufficiently concentrated (over about 1-2%).

Make 5% and 50% solutions of gum arabic by prolonged soaking and stirring of the gum in cold water. Compare the viscosities of these solutions, cold and hot. Evidently, viscosity is increased by concentration and low temperature, both of which tend to increase molecular aggregation and thus increase the *internal friction*, which is responsible for viscosity. (If particles get too large, however, viscosity again falls—see p. 146.)

*Zone of Maximum Colloidality.* Mix about 5 parts by weight of starch into 100 parts of *cold* water (say a teaspoonful of starch to a large cup of water). Note that the viscosity of the *suspension* is not appreciably different from that of water.

Now, while stirring steadily, pour in some 10% lye solution, until the mixture begins to thicken and get clear. Cease adding lye and stir steadily until the thick mass becomes smooth and clear. Note how the viscosity increases as the lye bursts the starch grains and makes of them a *colloidal dispersion*. On prolonged stirring, the paste will get somewhat thinner.

Then add *enough* strong\* hydrochloric acid to neutralize the alkaline lye; this may be gauged by the paste becoming white and opaque. Add a little more acid to be sure that the mixture is well on the acid side, and then boil. On boiling, the acid hydrolyzes the starch into much more finely dispersed dextrans and sugars. Note how the viscosity falls as dispersion proceeds towards true or crystalloid dispersion. We have therefore run the gamut of viscosity thus:

Low Viscosity	High Viscosity	Low Viscosity
Suspension of starch (coarse dispersion).	Colloidal dispersion of starch (intermediate).	Crystalloid (sugar) and fine colloidal (dextrin) dispersion of split-up starch.

Obviously, *somewhere* in the colloidal range, there must be a *zone* (or point) where the viscosity is a maximum. This may be observed by careful watching.

*Swelling.* Break up a *sheet* of gelatin into several pieces, which will have the same initial thickness. Immerse one piece of each of the following: distilled water; tap water;  $\frac{1}{2}\%$  hydrochloric acid; 5% hydrochloric acid;  $\frac{1}{2}\%$  hydrochloric acid + ordinary salt (about 5%);  $\frac{1}{2}\%$  lye solution. Allow to stand over night.

Note that the gelatin swells more in weak acid and in weak alkali than in pure water. Salts and stronger acid depress the swelling.

Fibrin is much more sensitive than gelatin in this respect, and shows marked swelling differences with small differences in the composition of the water bath—*e.g.*, it swells much more in

\* If weak acid be used, the paste is thinned by the contained water.

ordinary distilled water (which has a pH of about 5.5 due to absorption of atmospheric carbonic acid) than in *freshly* distilled water (pH about 7).

## V. ADSORPTION

*Liquid Solid.* (1) Wash some bits of white woolen cloth (flannel) or yarn thoroughly with soap and warm water, and rinse well. Then drop them into a warm *dilute* solution of green (malachite green) or violet (methyl violet) ink, and note that much of the color, *but not all*, is taken up by the wool, which becomes *dyed*. Try the same experiment with white washed silk. A *dilute* solution of any basic aniline dye (silk or wool dyes) may be used. Dyeing takes *time*; therefore early removal from the dye bath gives a lighter shade on the cloth.

Dyes may generally be abstracted from their solutions by charcoal, which, when washed, will not give up the color to water, but will give it up to alcohol. This solvent also "strips" many colors from silk or from glass or porcelain. Observe the effect of *very small* \* additions of acid (hydrochloric) and alkali (lye) on the adsorption of the dye by wool, silk, or charcoal.

(2) Cut up a thoroughly "dirty" dust rag, after having shaken out all loose dust, and place pieces in (a) plain water, (b) vinegar-water, (c) ammonia or borax-water, (d) soap-water. Note how the soap and the alkalies free the firmly held "adsorbed" dirt from the fabric. Heat helps the process.

Obviously, adsorption is a reversible process, and therefore tends to reach an equilibrium; so that while *more* dye may be adsorbed from a strong solution than from a weaker one, a *larger percentage* of dye is adsorbed from the weaker solution.

*Liquid/Liquid.* Shake a little lamp black or carbon black (soot will serve) with a mixture of water and carbon tetrachloride (Carbena will do). Note that the carbon remains with the heavy bottom layer of tetrachloride when the two immiscible liquids separate. On the other hand, if we use clay instead of lamp black, the clay will remain with the water. With a mixture of clay and lamp black, we may effect a separation of the two. Observe the effect of the mixed solvents on powdered galena

---

\* Stronger lye will dissolve wool and silk, but not cotton. Therefore if an "all wool" cloth leaves a residual lot of fiber in strong lye, we suspect the seller of error.

(lead sulphide), flowers of sulphur, and copper sulphide, and then read the section on "Flotation" (p. 201).

*Liquid/Gas.* (1) Mix some soap powder or soap into hot water, and beat up a good "suds." Skim off these "suds," and repeat the operation again and again. Finally, no more suds will form, because the soap is selectively adsorbed at the air/water interface of the suds bubbles, and is thus gradually removed.

(2) Hold a poker or other bit of soft iron pointing north and south, with an inclination or "dip" that will direct it toward the earth's magnetic pole (about  $45^\circ$  dip in temperate latitudes). Then hit it sharply several times with a hammer (this tends to make the poker, temporarily at least, magnetic). Now rub *one end* of a thin sewing needle from the *center* of the poker to one end of the poker, repeating this about a dozen times (this tends to magnetize the sewing needle).

Next coat the needle with a thin film of vaseline or grease—enough may generally be secured by wiping the finger alongside the nose—and carefully *float* the needle on a full glass or cup of cold water. The surface tension between the water, the air, and the adsorbed film of grease is sufficient to make the needle float. If the magnetization has been successful (as is generally the case), the needle will slowly point north and south, thus serving as a *household compass*. It may be made to follow any nearby piece of iron, just like a compass-needle (R. Ogden Doremus).

*Colloidal Protection.* Make the experiments with silver nitrate as explained on page 155, and see the effects of ordinary and of double colloidal protection.

Use distilled water, as most tap waters contain some chlorides.

## VI. ELECTRIC PROPERTIES

*Electrophoresis.* Join a strip or rod of clean zinc to a strip or rod of clean copper by a bit of copper wire in tight electric connection. Immerse this "electric couple" in various colloidal solutions, preferably faintly acid ones, and see if there is not an accumulation of the dispersed material at either "pole." Positively charged particles go to the copper; negatively charged ones to the zinc.

Any small dry cell may be employed to supply the necessary potential (current).

*Precipitation of Oppositely Charged Colloids.* The dispersed particles in ferric hydroxid sol (colloidal iron oxide) are positively charged, while those in gum mastic sol (see p. 132) or in gum arabic solution are negatively charged. Therefore colloidal iron oxide will precipitate mastic sol, and *vice versa*. The iron sol will also precipitate gum arabic solution, *unless too much gum is added all at once*; for the excess of gum then acts as a colloidal protector towards the newly forming precipitate, and keeps it in colloidal state, thus preventing it from settling out.



## BIBLIOGRAPHY

The number of books dealing with colloid chemistry and its applications has now become so great and is increasing so rapidly, that no adequate or lasting list can be prepared. Practically all of such books may be found by referring to the annual and the collective indexes of the principal chemical and physical journals, *e.g.*, *Chemical Abstracts*, *British Chemical Abstracts*, *Chimie et Industrie*, *Kolloid Zeitschrift*, *Journal of Physical Chemistry*, *Transactions of the Faraday Society*. The journal indexes will also give references to the multitude of paper dealing with colloidal phenomena, many of which are listed under special headings, *e.g.*, Adsorption, Coagulation, Deflocculation, Diffusion, Emulsions, Gels, Gelatin, Sols, and a wide variety of physical, chemical, biological and technical topics.

Below is given a list of the 202 papers published in the four volumes of Alexander's "Colloid Chemistry, Theoretical and Applied" (Chemical Catalog Co., 1926-32). Most of these papers contain references to numerous books and articles which are germane to their respective titles—in fact, one paper has over 1,000 such references.

The general reader, as well as the student, must select such publications as will appeal to him. There is no substitute for a personal acquaintance with books, gained in the library or at the booksellers.

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## GLOSSARY

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For the convenience of the reader, some of the less common terms employed by colloid chemists are here collected and briefly defined. Many other words are defined in the text at places identified in the Index.

- absorption*—passage of a liquid into the pores of a solid or a gel by the action of capillarity; e.g., water by a sponge, ink by blotting paper.
- adsorption*—binding of a finely divided substance (a gas, liquid or colloidal dispersion) to a surface.
- allocolloid*—one allotrope colloiddally dispersed in another, e.g., as with sulphur.
- amicon*—a particle invisible in the ultramicroscope, usually less than about 5  $\mu$  in diameter.
- blastula*—an early stage of embryos, the cellular mass being approximately spherical. A hollow center is a *blastocoele*; but where the cell-mass is solid, it is termed a *morula* (mulberry mass).
- botryoidal*—having the shape of a bunch of grapes.
- chloroplasts*—organized cellular units, or plastids, containing chlorophyl.
- chromocenter*—the small disc uniting salivary chromosomes.
- colloid*—any substance when dispersed into particles whose dimensions may vary between the approximate limits 5  $\mu$  and 100  $\mu$ . The individual particles may be tiny crystals, or partially oriented, or haphazard, random or amorphous groups; or mixtures of these may coexist. Fineness of dispersion is the critical factor, but its effects are not limited to the dimensions stated.
- conchoidal*—having shell-like depressions or elevations; commonly applied to the fracture of minerals.
- conjugation*—(*cytology*) side-by-side arrangement, or *synapsis*, of homologous chromosomes, as in cell-division.
- deflocculation*—dispersion of aggregates or flocculates.
- degree of freedom*—in a system of phases, the number of variables, e.g., temperature, pressure, concentration, which can be changed independently without eliminating any of the phases.
- emulsion*—a fine dispersion of one liquid in another. The dispersed particles may or may not be of colloidal size; if not they usually separate on standing long enough.
- emulsoid*—a colloid dispersion in which both phases are a liquid.
- gel*—an aggregation of colloidal particles into practically non-motile larger groups. Internal readjustment may cause syneresis (q.v.).
- gley* (*glei*)—a more or less sticky compact loam or clay parent substance found in moist soil conditions, as in moors (see J. S. Joffe, *Soil Science*, 1935, 39, 391).
- guttulate*—dropwise; in discrete drops.
- hydrophile*—literally “water-loving”; applied to colloids which tend to remain dispersed, hold water or remain in solution (see lyophile).
- hydrophobe*—literally “water-hating”; applied to colloids which tend to aggregate and shed water, or fall out of solution (see lyophobe).
- hysteresis*—time-lag in the aggregation of colloidal particles.
- interface*—the surface between two phases.
- irreversible*—a colloidal dispersion that will not redisperse after desiccation at ordinary temperatures.
- isocolloid*—a substance colloiddally dispersed in itself, e.g., as colloidal ice in water.
- isotherm*—a curve running through points determined by keeping the temperature constant, while some other factor, e.g., concentration, is varied.
- lathyrism*—a disease following the eating of certain species of peas (*lathyrus*).

*Liesegang's rings*—bands or rings usually regularly or rhythmically placed, which form when precipitates are produced by diffusion in jellies or similar structures.

*lyophile*—literally "solution-loving"; same as hydrophile, but also applicable to dispersion media other than water.

*lyophobe*—literally "solution-hating"; same as hydrophobe, but also applicable to dispersion media other than water.

*metastasis*—change of state.

*micron* ( $\mu$ )— $\frac{1}{1,000}$  mm.

*milli-micron* ( $m\mu$ )— $\frac{1}{1,000} \mu = \frac{1}{1,000,000}$  mm.  $\approx 10 \text{ \AA}$ .

*mitochondria*—a special form of granule-like bodies of lipid nature observable generally in cells after appropriate staining.

*orientation*—disposition in space or on a surface, relative to certain points, lines or surfaces. Opposed to molecular chaos.

*oxytocic*—promoting uterine contraction.

*pectisation*—gelatinization; an aggregation of colloidal particles into masses of sufficient size to be substantially devoid of Brownian motion, the resulting mass forming a flocculent precipitate, gel, or jelly, according to conditions.

*peptisation*—the reversal of pectization; the dispersion of a solid colloid by an enzyme (e.g., pepsin, whence the term) or by simple action of a dispersing agent (e.g., of  $\text{FeCl}_3$  gel by traces of  $\text{HCl}$ ,  $\text{SiO}_2$  gel by traces of  $\text{NaOH}$ ), or by heat (gelatin).

*phase*—a portion of matter regarded as homogeneous and separated from other differently constituted portions by demonstrable boundaries.

*protection*—inhibition of aggregation.

*protector*—a substance, usually a reversible colloid, which prevents or tends to prevent the aggregation of colloidal particles.

*reversible*—a reversible colloid is one that redissolves after desiccation at ordinary temperatures.

*sol*—a colloidal dispersion whose particles have sufficient Brownian motion to keep them in solution. The dispersing medium is often employed as a prefix: e.g.,

hydrosol = in water

sulphosol = " $\text{H}_2\text{SO}_4$

alcosol = " $\text{C}_2\text{H}_5\text{OH}$

aerosol = "air

pyrosol = "a melt (glass, metal, etc.).

*specific surface*—external, free, or rind surface per unit wt.

*stoichiometric*—having always the same regular proportions.

*submicron*—ultramicro.

*suspensoid*—a colloid in which the dispersed phase is a solid.

*syneresis*—drawing together of particles in a gel, with incidental liberation of liquid.

*thixotropy*—fluidification of a gel by mechanical agitation.

*trembles*—"milk-sickness" of cattle.

*ultrafiltration*—filtration (usually under pressure) through very close pored gels or jelly septa.

*ultramicro*—a sub-microscopic particle visible in an ultramicroscope.

*ultramicroscope*—a compound microscope having a dark field and means of intense illumination of the object to be examined by a beam of light preferably at right angles to the optical axis of the microscope. Particles are thus seen by the light they diffract.

*zygote*—the cell produced by the union of two cells (*gametes*) in reproduction; also applied to the individual developing therefrom.



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